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LXX. *Electrodeless Discharges.* By J. S. TOWNSEND, M.A.,  
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1. **I**N previous papers on high-frequency discharges I have shown that the theory which I gave to explain the uniform positive column in direct-current discharges† also explains the uniform luminous column of high-frequency discharges in cylindrical tubes.

The theory may be applied in general to various other types of discharge, such as electrodeless discharges in spherical bulbs, provided the pressure of the gas is within certain limits.

The experiments on direct-current discharges show that the force in the uniform positive column is independent of the current, when the increase of temperature of the gas due to the current is negligible. It is therefore necessary to assume that the numbers of electrons and positive ions per cubic centimetre of the gas are proportional to the current. It is also assumed that the supply of electrons and positive ions is maintained by the process of ionization by collision at a rate proportional to the number of electrons per cubic centimetre. In the steady state the rates at which the electrons and positive ions disappear from the gas are

\* Communicated by the Author.

† 'Electricity in Gases Section,' p. 302 (1915).

also proportional to the current, since these rates must be the same as the rate of ionization.

The effect of recombination of electrons and positive ions in the gas is small and may be neglected, since the rate at which electrons and positive ions disappear due to this process is proportional to the square of the current. According to this theory the electrons and positive ions disappear by diffusing to the sides of the tube.

2. In order to apply the theory to electrodeless discharges in a spherical bulb it may be supposed that the bulb is placed midway between two large parallel plates connected to the ends of the inductance of an oscillatory circuit which performs oscillations of constant amplitude.

When a continuous oscillatory discharge is thus maintained in the bulb, the oscillating force  $Z$  in the gas is less than the mean force  $V/b$  between the plates,  $V$  being the oscillating potential and  $b$  the distance between the plates. The difference between these forces depends on the current.

As in the ordinary uniform columns, it may be assumed that the effect of recombination may be neglected and that the force  $Z$  is independent of the amplitude of the current through the gas, but the difference between the forces  $Z$  and  $V/b$  increases with the current.

3. The theoretical investigation of high-frequency discharges involves several coefficients which depend on the energy of agitation of the electrons. Under certain conditions, depending on the pressure  $p$  of the gas and the periodic time  $T$  of the oscillations, there may be appreciable periodic variations in the energy of the electrons but in general these variations are small, and the mean values of the coefficients, which are independent of the time, may be used in the equations of motion.

Let  $K_1$  be the coefficient of diffusion of the electrons,  $w_1 Z$  the velocity in the direction of the electric force,  $K_1$  and  $w_1$  being the mean values of the coefficients during the time  $T$ . Let  $K_2$  and  $w_2$  be the corresponding coefficients for positive ions.

The electrons perform oscillations about their mean positions under the action of the force  $Z$  and the distances  $z_1$  traversed by the electrons on either side of their mean positions is  $w_1 Z_1 T / 2\pi$  where  $Z_1$  is the amplitude of the force  $Z$ .

In discharges in helium and neon at pressures of about 5 mm. the velocity  $w_1 Z_1$  is of the order  $10^8$  cm. per second, so that if the wave-length of the oscillations be about

100 metres the distance  $z_1$  is about half a millimetre. The corresponding distance traversed by the positive ions is negligible. Thus in spheres of diameter of about 8 cm. the rate at which the electrons are brought into contact with the surface by the oscillatory motion is very small. In tubes the rate at which electrons come into contact with the surface depends on the inclination of the force  $Z$  to the axis. This was observed by Gill and Donaldson in tubes 3 cm. in diameter containing air at low pressures\*. They found that the loss of conductivity due to this cause was greatest when the force was perpendicular to the axis. In the following theory this effect will be neglected, and it will be supposed that the electrons and positive ions come into contact with the surface of the bulb by the process of diffusion.

4. Let  $n_1$  be the number of electrons per cubic centimetre of the gas when the electrons are in their mean positions,  $a$  the radius of the bulb, and  $r$  the distance of a point in the gas from the centre of the bulb. The electrons are distributed symmetrically about the centre so that  $n_1$  is a function of  $r$  except at points near the surface of the bulb. Let  $N_1$  be the number of electrons in the sphere of radius  $r$ ,

$$N_1 = 4\pi \int_0^r n_1 r^2 dr,$$

and let  $n_2$  and  $N_2$  be the corresponding numbers of positive ions.

In the high-frequency discharges which are here considered the electric force is comparatively small and the mean velocity of the electrons in the direction of the electric force is small compared with the velocity of agitation. The rate at which molecules of the gas are ionized therefore depends on the energy of agitation of the electrons. Thus the mean rate of ionization in unit volume of the gas during the time  $T$  is proportional to the number of electrons  $n_1$  and to a factor which is a function of the mean energy of agitation  $E_1$ . The rate of increase of  $n_1$  may therefore be expressed in the form  $n_1\phi(E_1)$ . For the purposes of this investigation it is convenient to express  $n_1\phi(E_1)$  in terms of the electric force and the ordinary coefficient of ionization  $\alpha$ .

5. In the method of measuring this coefficient which is usually adopted electrons are set free from a plate  $P_1$  by the

\* E. W. B. Gill and R. H. Donaldson, *Phil. Mag.* xii. p. 719 (Sept. 1931).



action of ultra-violet light, and move under a constant force  $Z$  through a distance  $z$  to a parallel plate  $P_2$ . The increase in the number of electrons  $n$  that arrive at the plate  $P_2$  due to an increase  $dz$  in the distance between the plates is expressed in terms of  $\alpha$  by the equation  $dn = \alpha n dz$ . Thus the rate of increase of the number  $n$  in the time  $dt$  is  $\alpha n dz/dt$  where  $dz/dt$  is the velocity  $wZ$  of the electrons in the direction of the force. The rate of increase of  $n$  due to ionization by collision may therefore be expressed in the form  $\alpha n w Z$ .

It will be shown that the mean energy of agitation of the electrons in an oscillating discharge is the same as the mean energy  $E_1$  of electrons moving under a constant force of intensity  $Z_1/\sqrt{2}$ ,  $Z_1$  being the amplitude of the oscillating force.

When the ionization is maintained in a spherical bulb by an oscillating force the mean rate of ionization in a sphere of radius  $r$  may therefore be represented by the expression  $\alpha N_1 w_1 \bar{Z}$ , where  $\bar{Z}$  is the mean force  $Z_1/\sqrt{2}$ .

6. Since the electrons diffuse more rapidly than the positive ions the number of electrons left in the gas is less than the number of positive ions in the initial stages of the development of the current. There is therefore a positive charge in the gas giving rise to a force  $R$  along the radius, which retards the motion of the electrons and accelerates the motion of the positive ions towards the surface of the bulb ( $R = e(N_2 - N_1)/r^2$ ).

In general  $(N_2 - N_1)$  is small compared with  $N_1$  or  $N_2$ . In the steady state where the amplitude of the oscillating current is constant, the rates at which the electrons and positive ions pass outwards through the surface of a sphere of radius  $r$  is equal to the rate of ionization of the gas in the sphere. These conditions are expressed by the following equations:

$$\alpha N_1 w_1 \bar{Z} = -4\pi r^2 K_1 dn_1/dr - 4\pi r^2 n_1 w_1 R, \quad \dots \quad (1)$$

$$\alpha N_1 w_1 \bar{Z} = -4\pi r^2 K_2 dn_2/dr + 4\pi r^2 n_2 w_2 R. \quad \dots \quad (2)$$

If  $(n_2 - n_1)$  be neglected in comparison with  $n_1$  an equation is obtained for  $n_1$  by eliminating  $R$  which may be written in the form

$$\frac{d^2 n_1}{dr^2} + \frac{2}{r} \frac{dn_1}{dr} + c^2 n_1 = 0, \quad \dots \dots \dots (3)$$

where  $c^2$  is the constant  $\alpha w_1(w_1 + w_2)\bar{Z}/(K_1 w_2 + K_2 w_1)$ .

Since  $w_1$  is large compared with  $w_2$  and  $K_1 w_2$  large compared with  $K_2 w_1$ , the value of  $c^2$  is approximately

$$c^2 = \alpha w_1^2 \bar{Z} / K_1 w_2 \quad . \quad . \quad . \quad (4)$$

The solution of equation (3) is

$$n_1 = A \sin cr / cr \quad . \quad . \quad . \quad (5)$$

and for a first approximation this equation may be taken as

$$n_1 = A(1 - c^2 r^2 / 6) \quad . \quad . \quad . \quad (6)$$

$A$  being the value of  $n_1$  at the centre of the sphere. The total number of electrons in the sphere of radius  $r$  is

$$N_1 = \frac{4}{3} \pi r^3 A(1 - c^2 r^2 / 10) \quad . \quad . \quad . \quad (7)$$

Assuming the value of  $n_1$  near the surface of the sphere to be  $A/2$  the product  $c^2 a^2$  is 3, and the mean value of  $n_1$  throughout the gas is  $\cdot 7 A$ . If the ratio of the values of  $n_1$  at the centre and at the surface of the bulb, and the force  $\bar{Z}$  were known,  $\alpha$  would be determined by equation (4), since the coefficients  $w_1$ ,  $w_2$ , and  $K_1$  have been found in terms of the ratio  $\bar{Z}/p$ . The theory may thus be tested by comparing these values of  $\alpha$  with those found by the ordinary method\*.

7. Since  $K_1$  and  $w_1$  are large compared with  $K_2$  and  $w_2$ , the value of  $R$  is obtained directly from equations (1) and (2) without considering the solution given by equations (4), (5), and (6). The value of  $n_1$  is a maximum at the centre of the bulb so that  $dn_1/dr$  is negative. In equation (1) the quantity on the left is expressed as the difference of two large quantities, and in equation (2) the same quantity on the left is expressed as the sum of two small quantities. The first equation therefore shows that the two quantities on the right are approximately equal, so that the following equation is obtained for  $R$ :

$$R = -\frac{K_1}{w_1} \times \frac{1}{n_1} \times \frac{dn_1}{dr}, \quad . \quad . \quad . \quad (8)$$

and the difference between the potential at the centre and that at the surface of the bulb is

$$-\int_0^a R dr = (K_1 \log A/A^1)/w_1 \quad . \quad . \quad . \quad (9)$$

\* *Comptes Rendus*, clxxxvi. p. 55 (Jan. 1928).

According to the theory\* of the motion of electrons which has been given to explain the lateral diffusion of a stream, the ratio  $K_1/w_1$  is  $mu_1^2/3e$  where  $e$  is the atomic charge, so that if the kinetic energy of the electron be expressed in the form  $eE_1$  where  $E_1$  is a potential, the ratio  $K_1/w_1$  is  $2E_1/3$ , and the potential

$$-\int_0^a R dr \text{ is } (2E_1 \log A/A')/3.$$

If  $A'$  be one half of  $A$  this potential is  $\cdot 46 E_1$ .

Thus the potential  $\int_0^a R dr$  depends only on the energy of agitation of the electrons and on the ratio of the values of  $n_1$  at the centre and at the surface of the bulb †.

In ordinary discharge-tubes containing helium or neon at pressures exceeding 2 or 3 mm. the mean energy of agitation of the electrons is about 3 or 4 volts, so that the potential at the centre of the bulb exceeds that at the surface by about 1.5 or 2 volts.

The oscillating force increases with the pressure of the gas, and at high pressures (exceeding 2 or 3 mm.) the force  $R$  is small compared with the mean force  $\bar{Z}$ . At lower pressures the force  $R$  becomes comparable with the mean force  $\bar{Z}$ , so that it would be necessary to modify the theory in order to take into consideration the effect of the force  $R$  on the energy of agitation of the electrons.

8. The force  $R$  is not oscillatory, since the periodic variations in the numbers  $n_1$  and  $n_2$  are negligible. This may be seen by considering the rate of increase of  $n_1$  due to ionization by collision given by equation (1).

In discharges in helium in a tube 3 cm. in diameter, the value of  $\alpha$  is  $7.7 \times 10^{-3}$  when the pressure is 6 mm. and  $1.8 \times 10^{-3}$  when the pressure is 22 mm. ‡

The velocity  $w_1 \bar{Z}$  is of the order  $10^6$  cm. per second, so that the rate of increase of  $n_1$  due to ionization by

\* Proc. Roy. Soc. A, lxxxi. p. 464 (1908).

† A similar result is obtained for the uniform column of a discharge in a cylindrical tube. This may be deduced in the same way from equation (1), p. 1115, of the paper on "Uniform Columns in Electric Discharges" (Phil. Mag. vol. xi., May 1931). In this case also, the potential at the centre of a section exceeds that at the surface of the tube by the amount  $\cdot 46 E_1$  when the value of  $n_1$  near the surface is one half the value at the centre of a section.

‡ Phil. Mag. vol. xi. p. 1118 (May 1931).



collision is of the order  $5 \times 10^3 \times n_1$ . In the half period  $T/2$  of an oscillation of 100 metres in wave-length the number of electrons generated by collisions is therefore of the order  $n_1 \times 10^{-3}$ . This shows that during the time  $T$ , the periodic variations in the numbers  $n_1$  and  $n_2$  are very small so that the force  $R$  which depends on the difference may be considered constant for oscillations of wave-lengths of the order of 100 or 1000 metres.

9. Although the periodic changes in the numbers  $n_1$  and  $n_2$  are small there may be appreciable periodic changes in the energy of agitation of electrons.

In each complete oscillation there are two intervals during which the force is small, and the electrons lose more energy in collisions with molecules of the gas than they gain by moving in the direction of the force.

The periodic variations in the energy of agitation of the electrons arising from this cause depend on the mean free path of the electrons and on the mean loss of energy in a collision.

The calculation of the variations of energy is simplified by adopting the results of the investigations that have been made to determine the steady motion of electrons in a direct current moving under the action of a constant force. Let  $E_1$  be the mean energy of agitation of electrons in the steady motion maintained by a constant force of intensity  $\bar{Z}$ ,  $u_1$  the velocity  $\sqrt{2E_1/m}$ , and  $w_1\bar{Z}$  the velocity of the electrons in the direction of the force. The energy  $E_1$  and the velocity  $w_1\bar{Z}$ , have been determined experimentally for a large number of gases, and from these determinations the mean free path and the mean loss of energy of an electron in a collision are obtained by formulæ based on the kinetic theory of gases\*. These formulæ involve numerical coefficients which depend on the specification of a collision, and also on the distribution of the energies of the electrons about the mean energy.

Thus if  $l$  be the mean free path, and  $E$  the kinetic energy of an electron,  $\lambda E$  the mean loss of energy of the electron in a collision, and  $u$  the velocity  $\sqrt{2E/m}$ , the number of collisions made by the electron in the time  $dt$  is  $u dt/l$  and the loss of energy is  $\lambda E u dt/l$ . The mean loss of energy in the time  $dt$  of electrons in a stream where the energies are distributed about the mean energy  $E_1$  is therefore

\* 'Motion of Electrons in Gases' (Clarendon Press, Oxford, 1925).

$c_1 \lambda E_1 u_1 / l$ , where  $c_1$  is a constant depending on the distribution of the energies about the mean energy. The mean gain of energy in the time  $dt$  of the electrons in the stream due to the motion in the direction of the electric force is  $ew_1 \bar{Z}^2 dt$ . In the steady state where  $E_1$  is constant these two quantities are equal, so that the relation between the constants is given by the equation

$$2\lambda' E_1^2 / ml = ew_1 u_1 \bar{Z}^2, \dots \dots \dots (10)$$

where  $\lambda'$  is the product  $c_1 \lambda$ . The product  $w_1 u_1$  is a constant proportional to  $l$ .

10. The preceding results may be used in investigating the energy of agitation of the electrons in high-frequency discharges. In these cases it is necessary to consider the periodic variations in the energy. Let  $E$  be the mean energy at any time  $t$ ,  $u$  the velocity  $\sqrt{2E/m}$ ,  $wZ$  the velocity in the direction of the electric force,  $Z = Z_1 \sin qt$  the force, and  $T$  the periodic time  $2\pi/q$ . The coefficient  $w$  is inversely proportional to  $u$ , so that  $w_1 u_1 / u$  may be substituted for  $w$ . In this case the rate at which the mean energy of the electrons increases due to the motion in the direction of the force is  $ewZ^2$ , and the rate at which the mean energy is reduced by the collisions of the electrons with molecules is  $\lambda' Eu / l$ . The rate of change of the energy is the difference between these quantities, so that the equation \* for  $dE/dt$  is

$$u dE/dt = ew_1 u_1 Z^2 - \lambda' Eu^2 / l. \dots \dots (11)$$

which gives  $E$  in terms of  $t$  since  $u = \sqrt{2E/m}$ .

Substituting for  $Z^2$  its value  $\bar{Z}^2(1 - \cos 2qt)$  and for  $ew_1 u_1 \bar{Z}^2$  the value given by equation (10), the differential equation for  $E$  in terms of  $t$  becomes

$$\sqrt{2E/m} dE/dt = 2\lambda'(E_1^2(1 - \cos 2qt) - E^2) / lm. \dots (12)$$

Under an oscillating force of constant amplitude there is a steady state where the mean energy of the electrons may be expressed in the form of a series where one term is a constant and the other terms periodic functions of the time with constant amplitudes. The cases of particular interest are those where the amplitudes of the periodic terms are small compared with the constant term. Under these

\* This equation also gives the rate of change of the mean energy  $E$  of a group of electrons, moving in a uniform field where the force  $Z$  is constant, before the steady motion is attained,



conditions the solution of equation (12) representing the steady state is obtained by substituting  $E_1^2 + h$  for  $E^2$  where  $h$  is a function of the time. The following equation connecting  $E$ ,  $h$ , and  $t$ , is thus obtained :—

$$\sqrt{\frac{ml^2}{2\lambda^{12}E}} \frac{dh}{dt} + h = -E_1^2 \cos 2qt \quad . \quad . \quad (13)$$

If the variations in  $E$  be small compared with  $E_1$ ,  $E_1$  may be substituted for  $E$  in the first term of this equation, and since the first term is large compared with the second the function  $h$  is obtained in the simple form

$$h = -\frac{QE_1}{4\pi} \sin 2qt \quad . \quad . \quad . \quad (14)$$

where  $Q$  is the constant  $\lambda' u_1 E_1 T/l$ , which is the mean loss of energy of electrons in collisions with molecules of the gas during the time  $T$ . Thus  $E^2 = E_1^2 + h$ , and in cases where  $Q/4\pi$  is small compared with  $E_1$ , the energy  $E$  at any time is given by the equation

$$E = E_1 - (Q/8\pi) \sin 2qt \quad . \quad . \quad . \quad (15)$$

11. It will be noticed that the frequency of the periodic term is twice that of the oscillating force, and the mean values of  $E$  is the energy in a continuous current maintained by a constant force of intensity  $Z_1/\sqrt{2}^*$ .

The amplitude of the periodic term is small compared with  $E_1$  and may be neglected when the wave-length of the oscillations and the pressure of the gas are below certain limits.

The energy  $E_1$  is obtained directly in terms of the ratio  $\bar{Z}/p$  from experiments on the lateral diffusion of a stream of electrons, and the quantity  $Q$  may also be found directly from similar experiments, without considering the values of  $\lambda$  and  $l$ . The rate at which electrons lose energy in collisions with molecules in oscillatory currents is the same as in direct currents maintained by a constant force  $\bar{Z}$ , since the mean energy of agitation is the same in both cases. In direct currents when the motion is steady the amount of energy lost by electrons in collisions with molecules in the

\* On this point there is an error in the previous papers, where it is stated that the theory indicates that the effects obtained in oscillatory discharges are the same as those obtained in direct currents maintained by a constant force of intensity  $2Z_1/\pi$ .

time  $T$  is the same as the energy gained by moving the distance  $w_1 \bar{Z}T$  in the direction of the force. Thus the value of  $Q$  in volts is  $w_1 \bar{Z}^2 T$ .

In helium the energy of agitation  $E_1$  is  $2\bar{Z}/p$ , approximately, and the velocity  $w_1 \bar{Z}$ , is  $10^6 \sqrt{\bar{Z}/2p}$  cm. per sec. for values of  $\bar{Z}$  and  $p$  in ordinary uniform columns of discharges in wide tubes when the pressure is greater than 1 mm.,  $\bar{Z}$  being in volts per centimetre.

Under these conditions the value of  $Q$  in volts is  $10^6 \times p \cdot T \cdot E_1^{3/2}/4$ . The value of  $E_1$  depends on the diameter of the tube and on the pressure of the gas.

If  $E_1$  be 4 volts, the pressure of the gas 5 mm., and the wave-length of the oscillations 100 metres, the value of  $Q$  is  $\cdot 8 E_1$ .

Thus with oscillations of wave-lengths less than 100 metres, the periodic term is small compared with the constant  $E_1$  in discharges in helium at pressures less than 10 mm., and the mean values  $u_1$  and  $w_1$  may be used instead of  $u$  and  $w$  in considering the motion of the electrons.

In these cases the distribution of the energies of the electrons about the mean energy  $E_1$  in the oscillatory discharge should be the same as the distribution about the mean energy in a direct current maintained by a constant force of intensity  $Z_1/\sqrt{2}$ . The coefficient of ionization and the intensities of the principal lines in the spectrum of the gas should therefore be the same as the coefficient of ionization and the intensities of the lines in the direct current, since the rate of ionization and the intensity of the lines depend both on the value of the mean energy of the electron and on the distribution of the energies about the mean\*.

There is a large range of pressures and wave-lengths where this general agreement is obtained between oscillatory discharges and direct current discharges.

12. With large pressures and long wave-lengths the periodic variations in the energy of the electrons become appreciable. In addition to the corresponding periodic variations in the rate of ionization and in the intensity of the light there may also be changes in the mean values of these quantities, similar to those which would be obtained in a direct current if the distribution of the energies of the electrons about the mean energy were increased. In these

\* Phil. Mag. vol. ix. p. 1145 (June 1930).

discharges, therefore, the coefficient of ionization  $\alpha$  and the intensities of the lines in the spectrum of the gas would be somewhat greater than in a direct current maintained by a force  $Z$ .

It will be noticed that there are also lower limits to the pressures and wave-lengths for which the energy of the electrons in the oscillatory discharge is obtained accurately from equation (11). In that equation it is assumed that the velocity of the electrons in the direction of the oscillating force is proportional to  $Z$ . This implies that each electron makes several collisions with molecules in the time  $T$ . This condition is not satisfied with very short wave-lengths when the pressure is low and the mean free path is not small compared with the distance  $u_1 T$ . It may be generally assumed that equation (11) represents the value of  $dE/dt$  accurately when the wave-length of the oscillation exceeds 50 metres, and the pressure of the gas exceeds one-tenth of a millimetre.

13. In order to determine the mean energy of agitation in electrodeless discharges it is necessary to find the force in the gas. The simplest cases are those in which the gas is contained in a sphere or a long cylindrical tube placed midway between two parallel plates. The potential difference  $V$  between the plates may be measured experimentally, but the force  $Z$  in the gas differs both in amplitude and in phase from the mean force  $V/b$  between the plates,  $b$  being the distance between the plates. These differences are due to the periodic motion of the electrons under the action of the force  $Z$ . If  $z$  be the displacement of the electrons from their mean positions the velocity  $dz/dt$  is  $w_1 Z$ , and the distance  $z$  is  $-w_1 dZ/q^2 dt$ ,  $2\pi/q$  being the periodic time of the oscillations. The displacement  $z$  of the electrons is independent of the shape of the vessel containing the gas. For an approximate determination of the force  $Z$ , it may be assumed that the electrons are uniformly distributed in the gas.

14. If the gas be contained in a spherical bulb of radius  $a$  and  $B r^3$  the number of electrons in a sphere of radius  $r$ , the total charge on the electrons is  $-eBa^3$  and the centre of the distribution is at a distance  $z$  from the centre of the sphere. The displacement gives rise to a uniform force  $eBz$  in the gas in the direction normal to the plates, and outside the gas the force is the same as that due to positive and negative charges  $\pm eBa^3$  at points at a distance apart  $z$  and approximately at a distance  $b/2$  from the plates.



The force  $F$  due to the displacement of the electrons therefore comprises the term  $eBz$ , and, in addition, a number of terms representing the effect of the images of the charges  $\pm eBa^3$  in the plates. The principal images give rise to a force  $4eBza^3/b^3$  at the centre of the sphere, so that when  $b$  is greater than  $3a$  the value of  $F$  in the gas is approximately  $eBz(1-4a^3/b^3)$ .

In general the mean value of the force  $F$  in the gas may be expressed in the form

$$F = eB'z = eB'w_1dZ/q^2dt.$$

15. A similar result is obtained for discharges in cylindrical tubes when the axis of the tube is parallel to the plates, and midway between the plates. In this case, if  $r$  be the distance of a point in the gas from the axis of the tube,  $a$  the radius of the tube,  $B\pi^2$  the number of electrons in unit length of a cylinder of radius  $r$ , the mean positions of the electrons in sections of the tube at any time during the oscillations are along a line at a distance  $z$  from the axis of the tube. The principal term in the expression for the force  $F$  in gas due to the displacement of the electrons is  $2eBz$ , which represents a force proportional to  $z$ . The other terms are due to the images in the plates of a uniform distribution of positive electricity  $eBa^2$  per unit length, along the axis of the tube, and a similar distribution of negative electricity on a parallel line at a distance  $z$  from the axis. The principal images give rise to the force  $4eBza^2/b^2$ , so that when  $b$  is greater than  $3a$  the force  $F$  in the tube is  $2eBz(1-2a^2/b^2)$ , which may be written in the form  $eB'z$  or  $eB'w_1dZ/q^2dt$ , which is similar to the expression obtained for  $F$  in a spherical bulb.

15. In these cases the value of  $Z$  is obtained from the equation

$$Z = V/b - eB'w_1dZ/q^2dt, \quad . \quad . \quad . \quad (16)$$

from which the following relation is obtained between the amplitude  $Z_1$  and the amplitude  $V_1$  of the oscillatory potential

$$Z_1(1+T^2I^2)^{\frac{1}{2}} = V_1/b, \quad . \quad . \quad . \quad (17)$$

where  $I$  represents the quantity  $eB'w_1/2\pi$ , which is proportional to the number of electrons per cubic centimetre of the gas. The intensity of the light from the discharge is therefore proportional to  $I$ , so that  $I$  may be measured in

arbitrary units by a photoelectric cell. The value of  $Z_1$  is thus obtained from the values of  $I$  corresponding to different values of  $V_1$ .

Experiments are being made to determine the force by this method in gases at different pressures.

Equation 17 shows that in general if  $V_1$  be the potential difference between the external electrodes and  $b$  the distance between them,  $Z_1$  is less than  $V_1/b$ , but the difference diminishes with the current.

16. As the theory of radiation is related to the theory of conductivity it is of interest to consider some points which we observed in connexion with the different types of spectra obtained in helium at high pressures. They relate principally to the continuous spectrum and were not mentioned in the accounts of the experiments which we have already given.

In order to obtain a consistent explanation of the conductivity of a gas in the part of the discharge where the force is independent of the current, it is necessary to assume that the electrons do not recombine with the positive ions. This hypothesis is in agreement with the experiments which show that with small currents the intensity of the light from the uniform column of a discharge is proportional to the current. It thus appears that the simplest explanation of the radiation from the uniform column is that in which the light is attributed to collisions of electrons with atoms of the gas.

There are three types of spectra to be considered—the line spectrum, the band spectrum, and the continuous spectrum.

In high-frequency discharges the band spectrum in helium is seen with the line spectrum in spaces near the electrodes, and in continuous discharges in the negative glow, where there are several bright bands in the visible spectrum and the discharge has a bright purple colour\*.

It has been suggested that the bands are due to unstable molecules formed by the action of the discharge, but these investigations do not give direct evidence as to the origin of this spectrum, as the method of measuring the energies of the electrons does not apply to the electrons in the negative glow.

17. In tubes about 3 cm. in diameter the light in the positive column comprises only the line spectrum when the gas is at low pressures, but at pressures of 7 or 8 mm.

\* J. S. Townsend and S. P. McCallum, *Phil. Mag.* xiii. p. 1168 (Dec. 1931).

a continuous light is obtained in the visible spectrum which increases in intensity in comparison with the line spectrum as the pressure is increased. A few bands are also obtained in the positive column, but they are very faint.

In order to test whether the continuous spectrum was due to impurities the helium was admitted to a long quartz cylinder with parallel plate electrodes at one end. If the gas contained small traces of impurities they would be removed by passing an electrodeless discharge in the other end of the cylinder and the effect would be indicated by a large change in the sparking potential between the parallel plates. This method of testing for impurities has been found to be very sensitive\*.

In helium at high pressures the line spectrum and the continuous spectrum were observed in the electrodeless discharge, but the discharge had no effect on the sparking potential between the plates. It may therefore be concluded that the continuous spectrum is not due to impurities.

18. According to this theory, the change in the relative intensities of the continuous spectrum and the line spectrum obtained with a change of pressure is due to the energy of the electrons which excite the line spectrum being greater than the energy of those which excite the continuous spectrum.

When the pressure is increased the electric force required to maintain the discharge is also increased, but the ratio  $\bar{Z}/p$  diminishes. The proportion in which this ratio is changed is very small compared with the change of pressure. Thus, in tubes about 3 cm. in diameter, if the pressure of the helium be increased from 4 to 12 mm. the value of  $Z/p$  is reduced from 1.8 to 1.56 and the mean energy of agitation of the electrons is reduced from 3.6 volts to 3.1 volts. This reduction in the mean energy of agitation gives rise to a large reduction (about 6:1) in the number of electrons per cubic centimetre with the large energies required to excite the line spectrum when the same current flows through the gas.

The corresponding reduction in the number of electrons with the energies required to excite the continuous spectrum is much less.

Thus the intensity of the line spectrum diminishes in comparison with the continuous spectrum when the pressure is increased.

\* J. S. Townsend and S. P. McCallum, *Phil. Mag.* vi p. 858 (Nov. 1928).



In the experiments\* which were made to determine the intensity of the light in the visible spectrum of helium, the intensity was measured by a photoelectric cell, and light-filters were used in order to examine the changes of intensity in different parts of the spectrum due to changes of pressure.

The light passing through the filters included light in the different types of spectrum, so that the reduction in the photoelectric effect due to an increase of pressure was less than the reduction in the intensity of the light in the line spectrum. This may account for the fact that at the higher pressures from 13 to 38 mm. the reduction in the intensity of the photoelectric effect due to an increase of pressure was so small, and the energies of the electrons that excite the light which were calculated from the experiments are so much less than the values to be expected if all the light emitted from the discharge were in the line spectrum.

19. Further experiments have recently been made in which the photoelectric effect due to the ultra-violet spectrum was compared with the photoelectric effect due to the light in the visible spectrum from the same discharge. It has been found that the intensity of the green light diminishes in comparison with the ultra-violet as the pressure increases. This shows that the energies of the electrons which excite the ultra-violet light in helium at high pressures is less than the energies of those which excite the green light.

The explanation according to this theory is that the ultra-violet light contains a larger proportion of radiation in the continuous spectrum than the green light †.

The spectra of the discharges in the tubes which were used for these experiments have been photographed by Mr. Keyston. The tubes were in quartz, without electrodes, so that the gas should not become impure due to the long exposure required to obtain the photographs. The plates show the continuous spectrum in the ultra-violet region, which increases in intensity in comparison with the line spectrum, and becomes noticeable in the visible region as the pressure of the gas is increased. A set of photographs showing the effects obtained at different pressures will shortly be published.

\* J. S. Townsend and F. Llewellyn Jones, *Phil. Mag.* xii. p. 815 (Oct. 1931).

† These experiments have been made in collaboration with Mr. Pakala, and a more complete account of them will be given in another paper.

LXXI. *On Potential Dividers for Cathode Ray Oscillographs.* By F. P. BURCH, B.A., *Metropolitan-Vickers Electrical Company, Ltd., Manchester* \*.

SUMMARY.

IN Gábor's oscillographic method a known fraction of the voltage to be measured has to be transmitted over a long line and reproduced without distortion, the division of voltage being effected by condensers or condensers and resistances. If the low voltage impedance of the system is divided between the two ends of the line, the condensers may be made from six to eight times smaller than when it is concentrated at one end only. The field of application of the method is thus greatly extended.

I. *Introduction.*

THE principal problem of high speed cathode ray oscillography is that of recording on a stationary photographic film transients of which the moment of occurrence cannot be controlled. This has been solved in two ways. In the first, which may properly be associated with the name of Norinder†, the time-element of the record is introduced by making the cathode ray spot oscillate continually, at a known frequency, to and fro along the axis of abscissæ. To prevent fogging before the transient arrives, the beam is normally blocked by a target, and the transient is applied to a system of plates so arranged as to bend the beam past the target and cause it to reach the film with an ordinate deflexion proportional to the voltage. On the other hand, in the second method, introduced by Gábor‡, the time-motion is a single sweep of the beam across the film, once only. The transient is first made to operate a relay near the oscillograph, and then conveyed to the voltage deflexion plates by wires which are made long enough to delay its arrival until after the relay has released the beam from a "blocking chamber" and initiated the time-sweep.

For certain problems Norinder's system has very great advantages, but it gives no record of voltages near zero, and

\* Communicated by Sir J. J. Thomson, O.M., F.R.S.

† Norinder, *Zeits. f. Phys.* lxiii. p. 672 (1930).

‡ Gábor, 'Forschungshefte der Studiengesellschaft für Höchstspannungsanlagen,' Heft i. (1927).

the replotting of the oscillatory trace in Cartesian coordinates is a great trouble. Gábor's method is therefore being increasingly adopted, especially for high-voltage work. Its weakness, of course, lies in the energy required by the delay wires, which are indispensable if the start of the transient—nearly always the most interesting part—is to be recorded. When the voltage to be measured is of the same order as that required for the oscillograph deflexion (usually a few hundred volts\*), Gábor's method is only applicable to those problems in which the transmission of the entire transient over wires is required or can be tolerated. But when the voltage is high the delay wires can be connected to the tapping of a potential divider, and then under certain conditions the disturbance of the source becomes negligible. The nature of these conditions is most easily understood by considering the case in which the high voltage rises suddenly from zero to a constant value—the Heaviside "unit function." Faithful reproduction of this is a necessary and sufficient condition for faithful reproduction of any wave-form; the unit voltage function is therefore as important theoretically as its close realization is common in practice. To reproduce the sudden rise, a surge current of some 5 to 20 amperes must enter the delay wires. An initial current of at least this amount must therefore be drawn from the high-voltage source. Now in most problems the surge impedance of the high-voltage circuit is of the same order as that of the delay wires, so that at some hundreds or thousands of kilovolts the immediate effect of a load of several amperes is negligible. Accordingly the reproduction of a sudden rise, or a high-frequency change, usually presents no difficulty. But to reproduce a constant voltage, following a sudden rise, the current must continue for long enough to provide the whole charge required by the wires (a few microcoulombs, for a delay time of  $\frac{1}{2}$  micro-second) and, indeed, much more. For when we seek to limit the total charge taken from the high-voltage circuit, by including condensers in the potential divider, we find that it must always be fairly large compared with the charge on the wires, otherwise a sufficiently faithful reproduction cannot be obtained. Thus, if the capacity of the high-voltage circuit is limited, phenomena of moderate or long duration will be seriously affected. In most laboratory impulse circuits a drainage of 100 microcoulombs produces a considerable fall of voltage, and in many of the most interesting

\* In high speed work. For medium speeds amplifiers can be used; also the oscillograph can be made more sensitive.



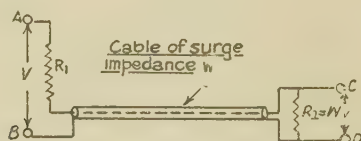
oscillographic problems, such as the study of the electromagnetic fields of thunderstorms, the quantity of electricity available is much smaller.

It is therefore important to cut down the capacities of the condensers in the potential divider to the minimum value consistent with reasonably faithful reproduction. In the present paper potential divider circuits are discussed in which they may be made over six times smaller than in the circuit used by Gábor. For some kinds of work, *e. g.*, the recording of surges on power transmission lines, condensers must in any case be included in the potential divider, to reduce the power current taken; and a minimum capacity is always desirable, not only electrically, but also because of the great bulk and cost of high-voltage condensers.

## II. *Types of Potential Divider.*

Fig. 1 shows the first and simplest potential divider system used by Gábor. The delay wires take the form of

Fig. 1.



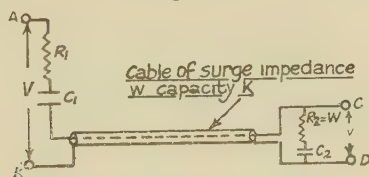
a concentric rubber insulated cable, commonly 50 yards long, in which the velocity of propagation is about half the speed of light. When the voltage across the terminals AB is suddenly raised from zero to unity, a wave enters the cable raising it to a voltage  $W/(R_1 + W)$ . On reaching the end CD it meets a resistance equal to the surge impedance  $W$  of the cable and accordingly suffers no reflexion. Thus the voltage across the terminals CD jumps suddenly from zero to  $W/(R_1 + W)$  and thereafter remains constant.

For cases where condensers must be included, Gábor used the circuit of fig. 2 with  $R_1 C_1$  approximately equal to  $W C_2$ ; and pointed out that  $C_2$  must be large compared with the capacity  $K$  of the cable, the error of reproduction being of order  $K/C_2$ .

The improvements to be described in this paper arose from the consideration of fig. 3, which is the simplest arrangement employing condensers, instead of resistances, to effect the initial division of potential. Under unit applied voltage a wave of magnitude  $C_1/2(C_1 + C_2)$  enters the cable and is

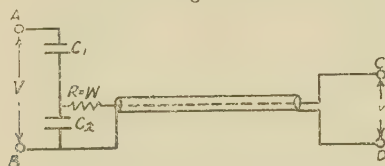
doubled by reflexion at CD, but is absorbed without sensible reflexion when it again reaches the input end. Thus the voltage at CD jumps initially to  $C_1/(C_1 + C_2)$ . But after

Fig. 2.



infinite time it has fallen to  $C_1/(C_1 + C_2 + K)$ ; as in fig. 2, there is an error of amount  $K/C_2$  ( $C_1$  being  $\ll C_2$ ). For the reduction of this error the circuit of fig. 4 suggested itself. Here a part of the low-voltage capacity has been transferred to the "receiving" end of the cable, being connected in series with a resistance  $W$  between the output terminals.

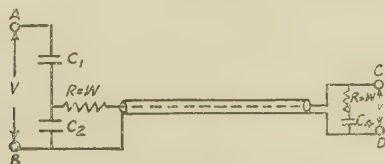
Fig. 3.



The "tailing off" of the first voltage wave, due to the charge drained from  $C_2$  by the cable, is now more or less compensated by the fact that  $C_1$  is simultaneously charging up. Moreover, if we make

$$C_1 + C_2 = C_4 + K$$

Fig. 4.



the initial value of output voltage will be the same as the value after infinite time. A very much more faithful reproduction may then be expected.

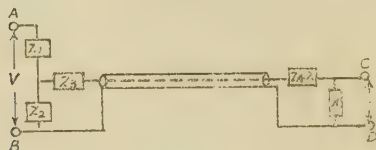
This principle of connecting shunt impedance across both ends of the cable, instead of only one, can of course be applied also to fig. 2. We will now discuss the performance of the various circuits mathematically.

### III. General Equations.

The application of Heaviside's methods to a line with terminal impedances has been explained by Carson\*. It will suffice here to give the principal formulæ, which we shall do for the rather general circuit of fig. 5. The output voltage  $v$ , due to an applied voltage  $V$ , is given by the solution of the operational equation

$$v = \frac{S \cdot e^{-p\tau}}{1 - \mu_1 \mu_2 e^{-2p\tau}} \cdot V, \quad \dots \quad (1)$$

Fig. 5.



in which

$$S = \frac{X}{Z_4} \cdot \frac{Z_2}{Z_1 + Z_2} \cdot \frac{(1 + \mu_1)(1 - \mu_2)}{2}, \quad \dots \quad (2)$$

$$\mu_1 = \frac{W(Z_1 + Z_2) - (Z_1 Z_2 + Z_2 Z_3 + Z_3 Z_1)}{W(Z_1 + Z_2) + (Z_1 Z_2 + Z_2 Z_3 + Z_3 Z_1)}, \quad \dots \quad (3)$$

$$\mu_2 = \frac{W - Z_4}{W + Z_4} \cdot \dots \quad (4)$$

The impedances  $X$ ,  $Z_1$ ,  $Z_2$ ,  $Z_3$ ,  $Z_4$ , and in general also the applied voltage  $V$ , are functions of the operator  $p = \frac{d}{dt}$ . The cable is assumed to be non-dissipative, and  $\tau = WK$  is the time taken by an electric wave to travel from one end to the other.

Equation (1) may also be written

$$v = V \cdot S \{ e^{-p\tau} + \mu_1 \mu_2 e^{-3p\tau} + (\mu_1 \mu_2)^2 e^{-5p\tau} + \dots \}, \quad \dots \quad (5)$$

\* Carson, 'Electric Circuit Theory and Operational Calculus,' McGraw Hill, Chap. X.



and the solution, giving  $v$  as a function of time, is

$$v = v_0(t - \tau) + v_1(t - 3\tau) + v_2(t - 5\tau) + \dots, \quad (6)$$

where  $v_0(t)$ ,  $v_1(t)$ , etc., are the solutions of the operational equations,

$$\left. \begin{aligned} v_0 &= S.V, \\ v_1 &= \mu_1 \mu_2 S.V, \\ v_2 &= (\mu_1 \mu_2)^2 S.V, \\ &\text{etc.} \end{aligned} \right\} \dots \dots \dots (7)$$

The terms of (6) represent, of course, the effects produced at the "receiving" end by the original wave and the successive reflected waves. For the most part we shall be interested in the response to a "unit voltage function," that is,  $V=0$  when  $t < 0$ ,  $V=1$  when  $t > 0$ , which may be called, following Carson, the "indicial response."

#### IV. Indicial Response of Simple Capacity Circuit.

For the circuit of fig. 3, writing

$$\left. \begin{aligned} \frac{1}{2W(C_1 + C_2)} &= \frac{K}{2(C_1 + C_2)} \cdot \frac{1}{\tau} = a, \\ m &= \frac{C_1}{C_1 + C_2}, \end{aligned} \right\} \dots \dots (8)$$

we have

$$S = m \cdot \frac{p}{p + a}, \quad \mu_1 = -\frac{a}{p + a}, \quad \mu_2 = -1. \quad (9)$$

The terms of the indicial response are

$$\left. \begin{aligned} v_0(\xi_0) &= m e^{-a\xi_0}, \\ v_1(\xi_1) &= m \cdot (a\xi_1) \cdot e^{-a\xi_1}, \\ v_n(\xi_n) &= m \cdot \frac{(a\xi_n)^n}{n!} e^{-a\xi_n}, \end{aligned} \right\} \xi_n = t - (2n + 1)\tau. \quad (10)$$

They are, of course, zero for negative values of  $\xi_n$ . Fig. 7 shows the result for the case

$$K/(C_1 + C_2) = \eta = 1/10;$$

the final value of output voltage,  $C_1/(C_1 + C_2 + K)$ , being taken as unity. It will be seen that there is a sharp discontinuity of slope at  $t=3\tau$ , but not elsewhere. The second reflected wave is inappreciable.

V. *Split Capacity Circuit.*

For this circuit (fig. 4) we take first the simplest case namely,

$$C_4/(C_1 + C_2) = f = 1.$$

Writing

$$\frac{1}{2W(C_1 + C_2)} = \frac{1}{2WC_4} = \frac{K}{(C_1 + C_2 + C_4)\tau} = a, \quad m_0 = \frac{C_1}{C_1 + C_2}, \quad \dots \dots (11)$$

we have

$$S = \frac{m_0}{2} \cdot \frac{p(p+2a)}{(p+a)^2}, \quad \mu_1 = \mu_2 = -\frac{a}{p+a}, \quad \dots (12)$$

and the terms of the indicial response are

$$\left. \begin{aligned} v_0(\xi_0) &= \frac{m_0}{2} e^{-a\xi_0} (1 + a\xi_0), \\ v_1(\xi_1) &= \frac{m_0}{2} \cdot \frac{(a\xi_1)^2}{2!} e^{-a\xi_1} \left(1 + \frac{a\xi_1}{3}\right), \\ v_n(\xi_n) &= \frac{m_0}{2} \cdot \frac{(a\xi_n)^{2n}}{(2n)!} e^{-a\xi_n} \left(1 + \frac{a\xi_n}{2n+1}\right), \end{aligned} \right\} \xi_n = t - (2n+1)\tau. \quad \dots \dots (13)$$

This is shown in fig. 7, for a total condenser capacity

$$C_1 + C_2 + C_4 = 10K,$$

as before ( $\eta=1/10$ ,  $f=1$ ). Though the initial error is, of course, just as great as with fig. 3, the fall of voltage is much more gradual, as was expected. There is now no discontinuity of slope anywhere; the existence of reflexions could not be inferred from the curve alone.

For the general case,

$$C_4/(C_1 + C_2) = f \neq 1,$$

we put

$$\frac{1}{2W(C_1 + C_2)} = a, \quad \frac{1}{2WC_4} = b, \quad \dots \dots (14)$$

and obtain

$$S = \frac{m_0}{2} \cdot \frac{p(p+2b)}{(p+a)(p+b)}, \quad \mu_1 = -\frac{a}{p+a}, \quad \mu_2 = -\frac{b}{p+b}. \quad \dots \dots (15)$$

The first three terms of the indicial response are

$$\begin{aligned}
 v_0(\xi_0) &= \frac{m_0}{2} \left\{ \frac{2b-a}{b-a} e^{-a\xi_0} - \frac{b}{b-a} e^{-b\xi_0} \right\}, \\
 v_1(\xi_1) &= \frac{m_0}{2} \left\{ \frac{ba(3b-a)}{(b-a)^3} (e^{-b\xi_1} - e^{-a\xi_1}) \right. \\
 &\quad \left. + \frac{b(2b-a)}{(b-a)^2} (a\xi_1) \cdot e^{-a\xi_1} + \frac{ba}{(b-a)^2} (b\xi_1) \cdot e^{-b\xi_1} \right\}, \\
 v_2(\xi_2) &= \frac{m_0}{2} \left\{ \frac{3b^2a^2(3b-a)}{(b-a)^5} (e^{-a\xi_2} - e^{-b\xi_2}) \right. \\
 &\quad - \frac{b^2a(5b-2a)}{(b-a)^4} (a\xi_2) e^{-a\xi_2} \\
 &\quad - \frac{ba^2(4b-a)}{(b-a)^4} (b\xi_2) e^{-b\xi_2} \\
 &\quad \left. + \frac{b^2(2b-a)}{(b-a)^3} \frac{(a\xi_2)^2}{2!} e^{-a\xi_2} - \frac{ba^2}{(b-a)^3} \cdot \frac{(b\xi_2)^2}{2!} e^{-b\xi_2} \right\}.
 \end{aligned} \tag{16}$$

If we make

$$C_1 + C_2 = C_4 + K,$$

to correct the "initial overshooting," we have, putting

$$\eta = K/(C_1 + C_2 + C_4),$$

$$a = \frac{\eta}{(1+\eta)\tau}, \quad b = \frac{\eta}{(1-\eta)\tau}, \quad f = \frac{1-\eta}{1+\eta}.$$

Fig. 7 shows the result for this case,  $\eta$  being 1/10 as before.

At  $t=7\tau$  one is dealing with the differences of numbers over 700, but calculation beyond  $7\tau$  is as unnecessary as it would be tedious. There is still no discontinuity of slope, and the maximum error is now only 1.6 per cent. To obtain an equally small error with the circuit of fig. 3 a total capacity

$$C_1 + C_2 = 62K$$

would be required, *i. e.*, 6.2 times larger than with fig. 4. The advantage of fig. 4 is even greater than this number suggests, for in practice one would make  $C_1 + C_2$  somewhat greater than  $C_4 + K$ , to distribute the error symmetrically about the final value; and this cannot be done with fig. 3.

VI. *Resistance-capacity Circuits.*

These are greatly to be preferred to the corresponding capacity circuits, figs. 3 and 4, primarily on account of their finite input impedance at infinite frequency, but also because they are capable of more accurate response curves.

For fig. 2, Gábor calculated the response up to  $5\tau$ , assuming

$$m_0 = W/(R_1 + W)$$

to be small, and

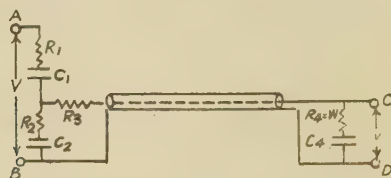
$$R_1 C_1 = W C_2.$$

The initial voltage is then  $m_0$  and the final voltage  $m_0/(1 + \eta)$ , where

$$\eta = K/(C_1 + C_2).$$

The voltage falls to  $m_0(1 - \eta)$  at  $t = 3\tau$ , passes through a minimum between  $t = 3\tau$  and  $t = 5\tau$ , and returns to  $m_0(1 - \eta)$

Fig. 6.



at  $t = 5\tau$ . The subsequent oscillations can be ignored. Thus the maximum error is  $\eta$  approximately. Gábor pointed out that if

$$R_1 C_1 = W C_2 (1 + \eta)$$

the initial value of voltage would be the same as the final value. It is easy to calculate that in this case the voltage at  $t = 3\tau$  is

$$m_0 \left[ 1 - \frac{\eta(1 - \eta)}{1 + \eta} \right] \text{ approximately.}$$

Clearly, a minimum total fluctuation roughly equal to  $\eta$  is the best that fig. 2 will give.

We shall not give the equations for fig. 2, but shall pass to the consideration of fig. 6. Here we have an extra condenser, so that in addition to making the initial voltage bear any desired ratio to the final voltage, we can satisfy some other condition for the improvement of the response. Further, we have included an extra resistance  $R_3$ , and, as



will appear later, still another possibility of improvement lies in the alteration of the ratio  $R_2 : R_3$ . We shall confine ourselves to cases in which the condition

$$R_3 + \frac{R_1 R_2}{R_1 + R_2} = W \quad . \quad . \quad . \quad . \quad (17)$$

is satisfied, so that the reflexion of very high frequencies is zero. Writing

$$\begin{aligned} \frac{1}{R_1 C_1} &= \alpha, & \frac{1}{R_2 C_2} &= \beta, & \frac{1}{W C_4} &= \gamma, \\ \frac{R_1}{R_1 + R_2} &= m_0, & 1 - \frac{R_3}{W} &= \kappa, & . \quad . \quad . \quad . \quad . \quad (18) \end{aligned}$$

$$\frac{K}{C_1 + C_2 + C_4} = \eta,$$

we have, taking (17) into account,

$$\mu_1 = - \frac{\kappa \{ p [m_0 \alpha + (1 - m_0) \beta] + \alpha \beta \}}{2p^2 + p \{ [(2 - \kappa)(1 - m_0) + \kappa] \alpha + [(2 - \kappa)m_0 + \kappa] \beta \} + \kappa \alpha \beta}, \quad (19)$$

while

$$\mu_2 = - \frac{\gamma}{2p + \gamma}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$\frac{Z_2}{Z_1 + Z_2} = m_0 \cdot \frac{p + \beta}{p + (1 - m_0) \alpha + m_0 \beta} \quad . \quad . \quad . \quad . \quad (21)$$

If  $m_0 \ll 1$ , (19) and (21) become, approximately

$$\mu_1 = - \frac{\kappa \beta}{2p + \kappa \beta}, \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$\frac{Z_2}{Z_1 + Z_2} = m_0 \frac{p + \beta}{p + \alpha}, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

so that

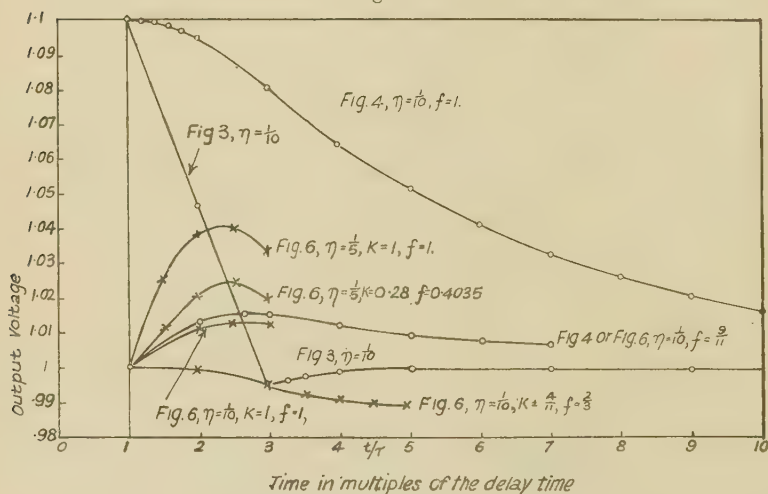
$$S = \frac{m_0}{2} \cdot \frac{p(p + \beta)(p + \gamma)}{(p + \alpha) \left( p + \frac{\kappa \beta}{2} \right) \left( p + \frac{\gamma}{2} \right)} \quad \text{approximately.} \quad (24)$$

We first notice that if  $\alpha = \beta$  the response functions take the same form as those of equations (15) and (16) and are, in fact, identical with them, for  $\kappa \beta$  is approximately equal to  $1/W(C_1 + C_2)$  and  $\gamma = 1/WC_4$ , while  $\alpha = \beta$  is equivalent

to  $m_0 = C_1/(C_1 + C_2)$ . The whole response is then the same, independently of the value of  $\kappa$ , as that of a split-capacity circuit (fig. 4) having the same values of capacity, and the curve of fig. 7 again serves for the case where  $\eta = 1/10$  and the initial overshooting is corrected.

$\alpha = \beta$  does not, however, represent the best that can be done. To obtain a general analytical expression for the conditions giving minimum error would be impracticable, but we shall obtain some insight into the possibilities by considering how far the initial rate of change of voltage and its

Fig. 7.



Response curves of potential dividers. Constant voltage suddenly applied.

derivative can be controlled. Dropping the scale factor  $m_0/2$  and writing (24) in the form

$$S = \frac{p(p+m)(p+n)}{(p+a)(p+b)(p+c)},$$

we have, operationally,

$$\begin{aligned} v_0'(t-\tau) &= \frac{d}{dt} v_0(t-\tau) = p S e^{-p\tau} \\ &= \frac{p^2(p+m)(p+n)}{(p+a)(p+b)(p+c)} \cdot e^{-p\tau}, \end{aligned}$$

and it is easy to show that

$$v_0'(0) = m+n-(a+b+c). \quad \dots \quad (25).$$

Similarly,

$$v_0''(0) = mn - (m+n)(a+b+c) + (a+b+c)^2 - (ab+bc+ca). \quad (26)$$

$\alpha$ ,  $\beta$ , and  $\gamma$  are connected with  $\tau$  through  $\eta$ ,  $\kappa$ , and  $m_0$  by the relation

$$\tau = \eta \left( \frac{m_0}{\kappa\alpha} + \frac{1-m_0}{\kappa\beta} + \frac{1}{\gamma} \right). \quad (27)$$

We shall be interested in cases in which  $\kappa\alpha$ ,  $\kappa\beta$ , and  $\gamma$  are of the same order of magnitude. (27) then becomes

$$\tau = \eta \cdot \frac{\kappa\beta + \gamma}{\kappa\beta\gamma}, \quad (28)$$

and if  $f = \kappa\beta/\gamma$  ( $= C_4/C_2$  approximately),

$$\left. \begin{aligned} \kappa\beta &= \frac{\eta}{\tau} (1+f), \\ \gamma &= \frac{\eta}{\tau} \left( 1 + \frac{1}{f} \right), \end{aligned} \right\} \quad (29)$$

We shall suppose that the initial overshooting is corrected; this requires

$$\frac{C_1}{C_1 + C_2 + C_4 + K} = \frac{m_0}{2},$$

which is equivalent to

$$\alpha = \frac{\beta\gamma[2-m_0(1+\eta)]}{(1+\eta)[\kappa\beta + (1-m_0)\gamma]}, \quad (30)$$

or, using (28), since  $m_0 \ll 1$ ,

$$\alpha = \frac{2\eta}{\kappa(1+\eta)\tau} \quad \text{approximately.} \quad (31)$$

Putting these values in (25) and (26), we obtain

$$\tau \cdot v_0'(0) = \frac{\eta}{2\kappa} \cdot \frac{(2-\kappa)f^2 - \frac{2(1-\eta)}{1+\eta} \cdot f + \kappa}{f}, \quad (32)$$

$$\begin{aligned} \tau^2 \cdot v_0''(0) &= \eta^2 \left[ \frac{\eta}{\kappa(1+\eta)} - \frac{1}{4} \right] \left( 2 + f + \frac{1}{f} \right) \\ &\quad - \left[ \frac{2\eta}{\kappa(1+\eta)} + \frac{\eta}{2} \left( 2 + f + \frac{1}{f} \right) \right] \cdot \tau \cdot v_0'(0). \end{aligned} \quad (33)$$

When  $\kappa > (1 - \sqrt{\eta})^2 / (1 + \eta)$ ,  $v_0'(0)$  is always positive. For a given value of  $\kappa$  it has a minimum value,

$$v_0'(0)_{\min.} = \eta \left\{ \sqrt{\frac{2 - \kappa}{\kappa}} - \frac{1 - \eta}{\kappa(1 + \eta)} \right\} \quad \text{when } f = \sqrt{\frac{\kappa}{2 - \kappa}}. \quad (34)$$

As  $\kappa$  diminishes from unity this minimum rises from

$$v_0'(0)_{\min.} = \frac{2\eta^2}{(1 + \eta)\tau} \quad \text{for } \kappa = 1, \quad f = 1 \quad (35)$$

up to a stationary value

$$v_0'(0)_{\min.} = \frac{2\eta^2}{(1 - \eta^2)\tau} \quad \text{for } \kappa = \frac{(1 - \eta)^2}{1 + \eta^2}, \quad f = \frac{1 - \eta}{1 + \eta}, \quad (36)$$

and then falls to

$$v_0'(0)_{\min.} = 0 \quad \text{for } \kappa = \frac{(1 - \sqrt{\eta})^2}{1 + \eta}, \quad f = \frac{1 - \sqrt{\eta}}{1 + \sqrt{\eta}}. \quad (37)$$

$f = (1 - \eta)/(1 + \eta)$  corresponds to  $\alpha = \beta$ , when

$$v_0'(0) = 2\eta^2/(1 - \eta^2)\tau$$

for all values of  $\kappa$ . If  $\kappa = 1$ , the best result is given by  $f = 1$ . Fig. 7 shows the first wave in this case, both for  $\eta = 1/10$  and also for  $\eta = 1/5$ . With  $\eta = 1/10$  the maximum error is 1.4 per cent., as compared with 1.6 per cent. when  $\alpha = \beta$ ; and even with  $\eta = 1/5$  the error is only 4.1 per cent.

However, if we are prepared to use small values of  $\kappa$ , we can do better still; in fact, if

$$\kappa < \frac{(1 - \sqrt{\eta})^2}{1 + \eta}, \quad (38)$$

$v_0'(0)$  vanishes for

$$f = \frac{1}{2 - \kappa} \left\{ \frac{1 - \eta}{1 + \eta} \pm \sqrt{\left( \frac{1 - \eta}{1 + \eta} \right)^2 - \kappa(2 - \kappa)} \right\} \quad (39)$$

Further, if  $\eta < 1/9$ , (38) is satisfied by

$$\kappa = \frac{4\eta}{1 + \eta},$$

and with this value of  $\kappa$ , if  $f$  is chosen to make  $v_0'(0)$  vanish,  $v_0''(0)$  vanishes also. The first two waves are given in fig. 7 for the case  $\eta = 1/10$ ,  $\kappa = 4\eta/(1 + \eta) = 4/11$ , and  $f = 2/3$ , corresponding to the positive sign in (39). The maximum



error is now  $-1.1$  per cent. approximately, occurring in the neighbourhood of  $t=5\tau$ .

Obviously some value of  $\kappa$  intermediate between  $4\eta/(1+\eta)$  and unity will give the best result. In the case  $\eta=1/10$ , the error could thus be brought down to a fraction of 1 per cent. But if we attempt to use larger values of  $\eta$ , the value of  $\kappa$  necessary to give a better result than  $\kappa=1$ ,  $f=1$  may become so small as to require an undesirably low high-voltage resistance  $R_1$ . To test this point the first wave has been calculated for  $\eta=1/5$ ,  $\kappa=0.28$ ,  $f=[\kappa/(2-\kappa)]^{1/2}=0.4035$ . It will be seen that the error is thus reduced from  $4.1$  per cent. to  $2.5$  per cent. Values of  $\kappa$  as low as  $0.28$  will often be permissible; to take a practical example, consider a potential divider to reduce from  $1,000,000$  volts to  $500$  volts, a ratio  $u$  of  $1/2000$ . If the surge impedance of the cable is  $50$  ohms, the circuit of fig. 2 has a resistance  $R_1=(1-u)W/u=99,950$  ohms, while fig. 6, with  $\kappa=0.28$ , requires  $R_1=\kappa W/2u=14,000$  ohms. If the surge impedance of the high-voltage circuit is, say,  $500$  ohms, this value of  $R_1$  is not unduly small. For a  $\frac{1}{2}$  microsecond delay time the capacity of the cable is  $K=\tau/W=0.01$  microfarad. Assuming the initial overshooting to be corrected in each case, fig. 2 requires, to limit the error to  $2.5$  per cent.,  $\eta=1/40$ ,  $C_1=200$  micromicrofarads approximately; while with fig. 6,  $\eta=1/5$ ,  $C_1=25$  micromicrofarads suffices. In cases where a high value of  $R_1$  is required, it will be best to make  $\kappa=1$ ,  $f=1$ , and distribute the error symmetrically by under-correcting the initial overshooting.

Results quite similar to the above are obtained if the resistance  $R_3$  is inserted at the "receiving" instead of the "sending" end, *i.e.*, in the position  $Z_4-X$  of fig. 5. But when  $R_1$  is small, *i.e.*,  $\kappa$  small, the arrangement of fig. 6 has the advantage that the cable is not subjected to a higher voltage than is required by the oscillograph. It is sometimes convenient on practical grounds to be able to use quite a low resistance  $R_1$ ; further, when  $R_1$  is low, the error caused by the stray capacities which are effectively in parallel with it is reduced.

Fig. 6 is, of course, very far from being the most general arrangement. Each of the impedances might consist of a quite complicated arrangement of resistances and condensers. I have not, however, investigated these possibilities; nor have I investigated the effect of departing from the condition (17). Such a departure ( $R_3=0$ ,  $R_2>W$ ) might be useful when a high value of  $R_1$ , together with a moderately high value of  $\eta$ , was required.

VII. *Response to Other Wave-Forms.*

It is of practical interest to consider how the errors affect the reproduction of other wave-forms. If a constant voltage is applied for a very short time,  $\delta t$ , and then removed, the output voltage rises at  $t=\tau$  to  $v_0(0)$ , but returns at  $t=\tau+\delta t$  to  $\delta t.v_0'(0)$  instead of zero, and the subsequent contribution of the first term is  $\delta t.v_0'(t-\tau)$ . To this is added, at  $t=3\tau$ , a square peak of amplitude  $v_1(0)$ , duration  $\delta t$ , followed by a contribution  $\delta t.v_1'(t-3\tau)$ ; and so on.

In practice, at least one end of the cable is made reflexion-free to high frequencies, so that  $v_1(0)$ ,  $v_2(0)$ , etc., are all zero, *i. e.*, the repetitions of the square peak do not occur.  $v_2'(0)$ ,  $v_3'(0)$ , etc., are also zero.  $\delta t.v_1'(0)$  vanishes if both ends are reflexion-free; otherwise there is a discontinuity of this amount at  $t=3\tau$ . Elsewhere there is a smooth fluctuation of voltage.

The steady state response to a sinusoidal e.m.f. is calculated by putting  $V=V_0e^{i\omega t}$  in equation (1), and writing  $i\omega$  instead of  $p$ . If  $S=G+iH$ ,  $\mu_1\mu_2=g+ih$ , we have

$$\left| \frac{v}{V_0} \right| = \frac{(G^2+H^2)^{\frac{1}{2}}}{(1+g^2+h^2-2g\cos 2\omega\tau-2h\sin 2\omega\tau)^{\frac{1}{2}}}.$$

For the circuits of fig. 4 or fig. 6, with  $\eta=1/10$ ,  $f=(1-\eta)/(1+\eta)$ , we calculate:

$2\pi/\omega\tau.$	$\left  \frac{v}{V_0} \right .$	$2\pi/\omega\tau.$	$\left  \frac{v}{V_0} \right .$
$\infty$	1	8/3	1.0056
20	1.0305	2	1.0009
11.1	1.0372	4/3	1.0023
9.884	1.0375	1	1.0001
8	1.0359	0	1
4	1.0198		

Thus the maximum error is 3.75 per cent., occurring, as might be expected, at a period  $2\pi/\omega$  equal not to some integral multiple of  $\tau$ , but to the resonant period of the condensers  $C_2$ ,  $C_4$  in series acting with the inductance  $W\tau$  of the cable ( $2\pi/\omega=9.884\tau$ ).

VIII. *Acknowledgement.*

I have great pleasure in thanking the Metropolitan-Vickers Electrical Co., Ltd., for permission to publish this paper

LXXII. *Some Experimental Support for Stern's Theory of the Electrolytic Double Layer.* By JOHN ST. LEGER PHILPOT, B.A. (from the Physical Chemistry Laboratory, Balliol and Trinity Colleges, Oxford).\*

INTRODUCTION.

THE special type of electrical double layer which exists between an electrode and a solution of an electrolyte has been called by Stern<sup>(1)</sup> an "electrolytic double

Fig. 1.

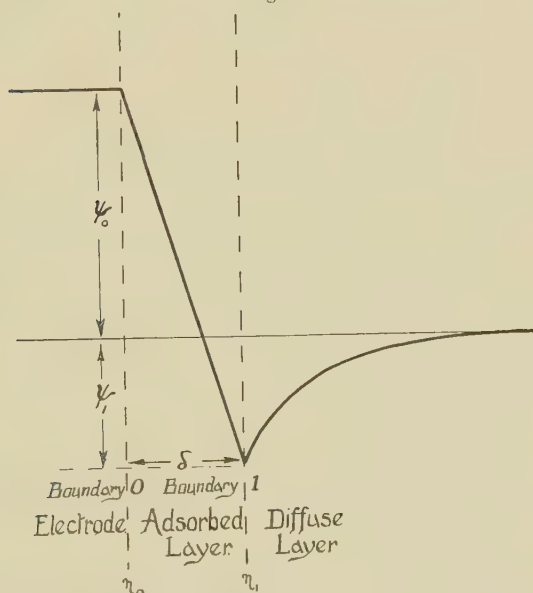


Diagram (after Stern) of an electrolytic double layer.

layer." Stern has studied theoretically the distribution of electrically charged particles in it. He represents his conception of the distribution by means of diagrams similar to that shown in fig. 1. The ordinates represent the electrical potential with respect to the interior of the solution, and the abscissæ represent the distance from a "boundary 0" defining the electrode surface. On the electrode side of

\* Communicated by Sir Harold Hartley, F.R.S.

boundary 0 the excess of positive over negative electricity is  $\eta_0$  per cm.<sup>2</sup>, assumed to be concentrated at boundary 0. On the solution side there is an "adsorbed" layer of ions, with net charge  $-\eta_1$ , assumed to be concentrated at boundary 1, distant  $\delta$  from boundary 0. Beyond this there is a "diffuse" layer, of net charge  $-\eta_2$ , arranged in an ion atmosphere whose charge density decreases rapidly as the distance from boundary 1 increases.

If the system as a whole is electrically neutral  $\eta_0 = \eta_1 + \eta_2$ . The electrical potentials are zero in the interior of the solution  $\psi_1$  at boundary 1, and  $\psi_0$  at boundary 0. The special case shown in fig. 1 is a complex one, where  $\eta_1$  is of opposite sign to  $\eta_2$  owing to "specific adsorption" of a negative ion. Stern's theory is a combination of the simple Helmholtz theory of the "adsorbed" layer, corresponding to  $\eta_2 = 0$ , and the Gouy-Chapman theory of the "diffuse" layer corresponding to  $\eta_1 = 0$ .

Making the above and some further assumptions, Stern has derived an equation connecting the potentials  $\psi_0$  and  $\psi_1$  with the charges  $\eta_0$ ,  $\eta_1$ , and  $-\eta_2$ . The experimental work described in the present paper provides support for the belief that Stern's theory and equation are fundamentally correct. The evidence is not, however, direct, since none of the quantities concerned are directly measurable. An understanding of the relation between the theoretically and experimentally accessible quantities requires a precision of definition which is not easily attained, and whose discussion must be postponed till a later paper. For the present it must suffice to state:—

(a) In a case where no charged particles can cross "boundary 0" (and not necessarily in any other), Stern's " $\eta_0$ " must be identical with the experimental quantity  $\epsilon$  which is defined below.

(b) When an electrode is such that over a large range of potential no electrochemical change can occur, there is considerable *a priori* justification for the belief that over part of this range no charged particles can cross boundary 0.

(c) Mercury in specially purified solutions of hydrochloric acid or sodium chloride, as used in the present work, forms a close approximation to such an electrode.

(d) The belief expressed in (b) is strengthened by the fact that  $\epsilon$ , measured on the electrode described in (c), varies with potential and concentration in the same way as in Stern's equation.



(e) The same fact provides evidence that Stern's equation is an approximation to the truth.

*Definition of  $\epsilon$  or  $\left(\frac{\partial q}{\partial s}\right)_{\psi_s}$ .*—Consider a pair of electrodes.

R and S, immersed in a solution of electrolyte, and connected with each other through an external circuit.

Electrode S is perfectly polarizable, *i. e.*, its electrical potential  $\psi_s$  is uniquely determined by its area S and by the quantity of electricity  $q$  which has flowed through the external circuit from R to S.

Electrode R is a non-polarizable "reference electrode," *i. e.*, its electrical potential  $\psi_R$  with respect to the solvent is independent of  $q$  and dependent only on the composition of the system.

If  $\psi_s$  is kept constant the current flowing from R to S is given by

$$\left(\frac{\partial q}{\partial t}\right)_{\psi_s} = \left(\frac{\partial q}{\partial s}\right)_{\psi_s} \frac{ds}{dt} \quad . \quad . \quad . \quad . \quad (1)$$

$\left(\frac{\partial q}{\partial s}\right)_{\psi_s}$  is the "capacity per unit of surface at constant

potential" as defined by Lippmann<sup>(11)</sup>, and is generally written  $\epsilon$  for short. At a perfectly polarizable electrode no continuous electrochemical change can occur. This is an

unattainable ideal, and for all actual electrodes  $\left(\frac{\partial q}{\partial s}\right)_{\psi_s}$  will

have a value greater than that for the corresponding ideal electrode. If  $q_a$  refers to an actual electrode and  $q_i$  and  $\epsilon_i$  to the corresponding ideal one, and if I is the current corresponding to unavoidable electrochemical change, then

$$\left(\frac{\partial q_a}{\partial t}\right)_{\psi_s} = \left(\frac{\partial q_i}{\partial s}\right)_{\psi_s} \frac{ds}{dt} + I = \epsilon_i \frac{ds}{dt} + I \quad . \quad . \quad . \quad (1a)$$

In the present work, I has been made quite small compared with  $\epsilon_i \frac{ds}{dt}$ , and a correction has been applied for what remains. Thus fairly reliable values for  $\epsilon_i$  have been obtained for comparison with  $\eta_0$ .

*Potentials.*—The potential  $\psi_s$  will, in the present paper, be identified with Stern's " $\psi_0$ ." This involves the acceptance of Stern's assumption that the charge on the electrode side is concentrated entirely at "boundary 0." The quantities " $\psi$ " are electrical potential differences between two phases, which according to Guggenheim<sup>(2), (3)</sup> have individually

no physical significance. The measured potential difference  $E$  is equal to  $\psi_R - \psi_S$ , if  $\psi_R$  is defined so as to include all liquid or metal junction potentials.

*Stern's equation.*—The theoretical equation derived by Stern is

$$K_0(\psi_0 - \psi_1) = FZ \left( \frac{1}{2 + \frac{1}{c} e^{\frac{\psi_- - F\psi_1}{RT}}} - \frac{1}{2 + \frac{1}{c} e^{\frac{\phi_+ + F\psi_1}{RT}}} \right) + \sqrt{\frac{DRTc}{2\pi \times 18}} \left( e^{\frac{F\psi_1}{2RT}} - e^{\frac{-F\psi_1}{2RT}} \right). \quad (2)$$

where the quantities  $\eta$  and  $\psi$  have been defined,

$K_0 = \frac{d}{4\pi\delta}$  = the capacity per cm.<sup>2</sup> of the "adsorbed" layer by virtue of its being separated from the electrode by a space of thickness  $\delta$  and dielectric constant  $d$ .

$F$  = the value of the Faraday in electrostatic units.

$Z$  = the number of moles on 1 cm.<sup>2</sup> area of water, assumed to equal  $1.7 \times 10^{-9}$ .

$\phi_+$  and  $\phi_-$  = the "specific adsorption potentials" of the ions defined as the free energy of formation of an "adsorbed layer" from one pole of positive or negative ion, respectively, under conditions where  $\psi_1 = 0$ .

$D$  = the dielectric constant of water.

$c$  = the concentration expressed as mole fraction.

$C$  will denote the concentration in moles per thousand grams and is equal to  $0.018c$  if the molecular weight of water is given its simple value 18.

The electrical quantities are expressed in absolute electrostatic units. Converting to practical electromagnetic units, replacing  $c$  by  $C$ , and inserting the values of the constants, transforms the equation to

$$\eta_0 = 8.15 \left( \frac{1}{2 + \frac{1}{0.036 C} e^{\frac{\phi_- - F\psi_1}{RT}}} - \frac{1}{2 + \frac{1}{0.036 C} e^{\frac{\phi_+ + F\psi_1}{RT}}} \right) + 5.73 \sqrt{C} \left( e^{\frac{F\psi_1}{2RT}} - e^{\frac{-F\psi_1}{2RT}} \right). \quad (2a)$$

$$= K_0(\psi_0 - \psi_1). \quad (3)$$

$\eta_0$  is now expressed in microcoulombs per cm.<sup>2</sup>,  $\psi_1$  and  $\psi_0$  in volts,  $\phi_+$  and  $\phi_-$  in joules per gram ion, and  $K_0$  in microfarads per cm.<sup>2</sup>

For values of  $\eta_0$  up to 10, and of  $C$  up to 0.1, which is the experimental range of the present work, the 2 in the denominators in equation (2a) can be neglected. Doing this, and writing

$$\begin{aligned} x &= e^{\frac{F\psi_1}{2RT}} & A &= 2.93 \\ X_+ &= e^{\frac{-\phi_+}{RT}} & B &= 5.73 \\ X_- &= e^{\frac{-\phi_-}{RT}} \end{aligned}$$

$$\eta_0 = \overbrace{AC\left(X_-x^2 - \frac{X_+}{x^2}\right)}^{\eta_1} + \overbrace{B\sqrt{C}\left(x - \frac{1}{x}\right)}^{\eta_2}. \quad (2b)$$

$\eta_0$  may be separated for mathematical convenience into  $\eta_+$  and  $\eta_-$ , the portions which correspond respectively to positive and negative ions on the solution side of boundary 0. Thus, within the present experimental range,

$$-\eta_+ = AC \frac{X_+}{x^2} + \frac{B\sqrt{C}}{x}. \quad (2b_+)$$

$$\eta_- = ACX_-x^2 + B\sqrt{C}x. \quad (2b_-)$$

When  $\psi_1$  is numerically large,  $X$  is much greater or smaller than 1, according to the sign of  $\psi_1$ .  $\eta_0$  then becomes equal to  $\eta_-$  and  $\eta_+$  in the two cases respectively.

It is readily deducible from Stern's equation that

$$\lim_{(\eta_0 \rightarrow \pm\infty)} \frac{d\eta_0}{d\psi_0} = K_0,$$

and that, for a constant and numerically large value of  $\eta_0$ ,

$$\psi_0 = \text{const.} \pm \frac{RT}{F} \log C,$$

the sign of  $\frac{RT}{F} \log C$  being opposite to that of  $\eta_0$ . In other words, the theoretical curve representing  $\eta_0$  in terms of  $\psi_0$ , has two nearly linear portions of slope approximately equal to  $K_0$ , which move apart along the axis of  $\eta_0$  with increasing dilution, at a rate of  $\frac{2RT}{F} \log C$ . They are joined by

a non-linear portion. This form of curve is peculiar to Stern's theory. By suitable adjustment of constants the linear or non-linear portions can be made to predominate, giving in the two limiting cases the wholly linear curve of the Helmholtz theory, and the wholly non-linear curve of the Chapman-Gouy theory.

Stern's equation in its present form applies only to univalent ions and to a constant value of  $K_0$ . Uni-univalent electrolytes were used in the present work, but it was found that  $K_0$  was different for the two ions. In applying Stern's equation, therefore, the value of  $K_0$  was chosen to correspond with the predominant ion, or if neither predominated, equation (3) was written

$$\psi_0 = \frac{\eta_+}{K_{0+}} + \frac{\eta_-}{K_{0-}} + \psi_1, \quad . \quad . \quad . \quad (3a)$$

where  $K_{0+}$  and  $K_{0-}$  are the values of  $K_0$  corresponding with each ion.

*The measurement of  $\epsilon$ .*—If a dropping mercury electrode is kept at a constant potential,  $\frac{ds}{dt}$  of equation (1a) can be identified with the area of fresh electrolytic double layer which is formed per second by the expanding drops, and this must equal the area of a drop at the moment of detachment multiplied by the number of drops per second. If  $r$  is the radius of a drop (assumed to be approximately spherical at the moment of detachment) and if  $x$  is the number of drops per second, then

$$\frac{ds}{dt} = 4\pi r^2 x.$$

If  $n$  drops fill a volume  $V$  in time  $T$ , then

$$r = \left( \frac{V}{\frac{4}{3}\pi n} \right)^{\frac{1}{3}}$$

and

$$x = \frac{n}{T}.$$

Hence, from equation (1a),

$$\epsilon_i = \left( \frac{\partial q_a}{\partial t} \right)_{\psi_s} \times \frac{I}{(4\pi)^{\frac{1}{3}} \left( \frac{V}{3} \right)^{\frac{2}{3}} n^{\frac{1}{3}}} - I. \quad . \quad . \quad (1b)$$

All the quantities on the right-hand side are directly



measurable except I. Heyrowsky <sup>(12)</sup> has shown that I, if small, is independent of potential except in the neighbourhood of the discharging potential of the substance undergoing electrochemical change. Therefore, if I is ignored the experimental curve of  $\epsilon$  against E will be shifted along the  $\epsilon$  axis without change of shape except in the neighbourhood of a discharging potential. Also it is fairly certain that

as  $\frac{ds}{dt}$  is increased the ratio of  $\epsilon \frac{ds}{dt}$  to I increases, so that for extremely high values of  $\frac{ds}{dt}$  I, is negligible in equation (1 b)

provided the concentration of reducible substances is small. enormous dropping-rates introduce difficulties in measuring

$\frac{ds}{dt}$ , but it is possible to measure the limiting value (as  $\frac{ds}{dt}$  increases) of the potential where  $\epsilon = 0$ . This is, in fact, Freundlich's "electrokinetic potential," relative to the reference electrode R.

$\epsilon_a$  can now be converted to  $\epsilon_i$ ; it is only necessary to plot  $\epsilon_a$  against E and shift the curve along the  $\epsilon$ -axis till it cuts the E-axis at the "electrokinetic potential." The extent of the shift is equal to I, and will be seen from figs. 5 and 6 to be quite small in the present case. The above correction is only valid at potentials between the electrokinetic potential and the discharging potential of a substance present. There is, however, no evidence for a discharging potential occurring over the range of the curves shown.

*Electrolytic purification.*—In the present work the final purification from reducible substances was done electrolytically in the cathode compartment of the cell itself. A pool of mercury was maintained at a potential sufficient to reduce impurities, but not hydrogen or sodium ions. Extremely efficient stirring was necessary, which was achieved by bubbling hydrogen under reduced pressure through the mercury. An estimate of the quantity of impurities reduced was obtained from the area under the curve, obtained by plotting current against time. The ratio of initial to final concentration of reducible impurities was found from the current required to maintain a stationary mercury surface at a given potential. Combination of these data gave absolute values for the initial and final concentrations, which were of the order  $10^{-7}$  and  $10^{-9}$  normal respectively.

## EXPERIMENTAL DETAILS.

*Water* was distilled at a pressure of 20 mm. in a stream of nitrogen and condensed on silica, the aim being to remove oxygen and other reducible impurities as completely as possible. The low temperature permitted the use of rubber bungs, which had been boiled in alkali and distilled water, dried, and soaked in molten paraffin wax for an hour. (The rubber imbibes the paraffin, which fills the pores and prevents the slow diffusion of sulphurous impurities from the interior). During the distillation samples were run into a test cell containing a gold cathode and platinum anode. Roughly speaking, the current at 1-volt applied potential was a measure of the reducible impurities and at 8 volts a measure of the ordinary conductivity. The water was collected when it gave below  $10^{-8}$  amp. for 1 volt and  $3 \times 10^{-6}$  amp. for 8 vols. (The cathode area was 5 cm.<sup>2</sup>). The specific conductivity of the yield as a whole was generally measured in an Ostwald cell and was from 2 to  $4 \times 10^{-7}$  reciprocal ohm.

*Hydrochloric acid.*—The gas was transferred *in vacuo* from the concentrated acid to pure water, after letting the first portion go to waste and filtering the gas through glass wool. The strong solution thus obtained was titrated, and diluted as required without contact with air.

*Sodium chloride.*—Some Kahlbaum *pro analysi* material was used without further purification.

*Mercury.*—The mercury was washed for 12 hours in an acid column with air-lift, and distilled in a Hulett still, with an air-stream at 40 mm. pressure. It was filtered through silk immediately before use.

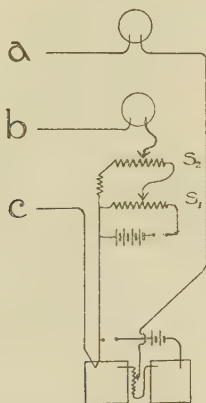
*Hydrogen.*—Cylinder hydrogen was passed over an incandescent tungsten filament, to remove oxygen, then through soda-lime, and filtered through a thick plug of glass wool.

*Handling of solutions.*—Water and solutions were stored, and dilutions made, in  $\frac{1}{2}$ -2-litre durosil flasks, fitted with paraffined rubber bungs (described above), containing tubes for filling, emptying, and evacuating or filling with hydrogen. For fear of a possible effect of traces of sodium and other ions on the measurements in hydrochloric acid, the flasks were coated inside with paraffin wax containing a minute trace of pure "crepe" rubber (free from sulphur). The paraffin was deposited as a thin layer from carbon tetrachloride solution and warmed in the air-oven; the trace of

rubber prevents flaking. As a precaution against contamination the coated flasks were left filled with distilled water for some hours before they were first used, but there was no detectable increase in either reducible impurity or conductivity of water kept for months in them. The results obtained with sodium chloride show that a trace of sodium ion would have no effect on measurements in hydrochloric acid, so the paraffin lining is unnecessary, at any rate if pyrex flasks are used.

The solutions on entering the cell contained apparently about the same amount of reducible impurity as those of Bowden and Rideal <sup>(5)</sup>, but more than those of Bowden <sup>(7)</sup> in

Fig. 2.



The electrical circuit :

*a*, to reference electrode ; *b*, to anode ; *c*, to cathode.

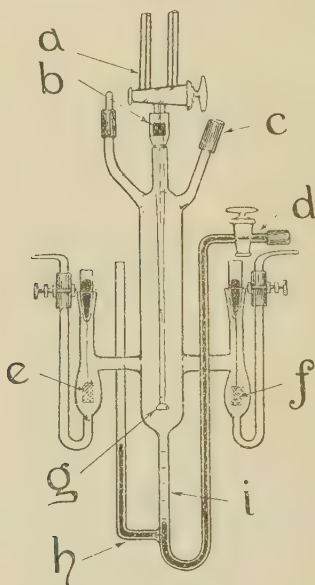
later work on overvoltage. In view of the success of the final electrolytic purification described above the sources of impurities were not investigated further.

*The electrical circuit.*—A wiring diagram is given in fig. 2. The potentiometer circuit was identical with that described by Nonhebel <sup>(8)</sup>. In the current circuit the only notable feature was the adjusting device consisting of two sliding resistances,  $S_1$  and  $S_2$ , and a hundred-ohm coil.  $S_1$  gave a coarse and  $S_2$  a fine adjustment of the applied potential, which was altered till the potentiometer was balanced at a chosen value. The potentiometer galvanometer was a mirror instrument sensitive to  $10^{-10}$  amp., while the currents were measured with a bifilar pointer instrument, with the smallest

division equal to  $5 \times 10^{-8}$  amp., which could be multiplied by 10 or 100, or 1000 by a universal shunt.

*The cell.*—The final form of cell is shown in fig. 3. The cathode compartment is a vertical cylinder ending in an outlet for mercury and solution, which has a straight graduated portion *i* and a platinum contact *h* at the bottom, and communicates through a tap *d* and rubber tube with an evacuated filter flask. The anode *f* (of silver gauze) and reference electrode *e* (electrolytic silver-silver chloride as

Fig. 3.



The cell.

- |  |   |
|--|---|
| <i>a.</i> Dropper bubbler tap.           | <i>f.</i> Anode                         |
| <i>b.</i> Contact for dropper.           | <i>g.</i> Dropper and bubbler.          |
| <i>c.</i> To pump or hydrogen train.     | <i>h.</i> Contact for bubbling cathode. |
| <i>d.</i> Exit for mercury and solution. | <i>i.</i> Graduated tube.               |
| <i>e.</i> Reference electrode.           |   |

described by Nonhebel <sup>(8)</sup> are in compartments on opposite sides of the cathode compartment and separated from it by perforated diaphragms, which give high conductivity while preventing mixing of unpurified solution with the purified contents of the cathode compartment. The anode and reference compartments have exit tubes for emptying, and the electrodes



themselves are fixed in by means of ground-glass joints. At the top of the cathode compartment are three tubes, one for filling with solution, another for admitting or removing hydrogen, while the third admits the combined dropping electrode and hydrogen bubbler. This consists of a fine-drawn capillary, ending in an inverted cup *g* at the bottom, and joined at the top to a two-way tap *a*, which admits either mercury, or hydrogen which has passed through a fine capillary, to control the rate. A platinum seal *b* provides contact with the drops. The inverted cup is a new type of dropper which gives large drops (about 3 mm. diameter), while allowing the capillary to be of such small bore (tapering slightly upwards) that solution does not creep up when the mercury is turned off. (The usual practice seems to be to use a capillary which tapers downwards. This not only gives drops too small for the present purpose, but also causes the dropping to be unstable below a critical rate.)

The "run" procedure with this cell was as follows:—After being cleaned with nitric and chromic mixture and rinsed finally with the solution to be used, the cell was immersed in the thermostat (paraffin,  $25^{\circ}\text{C.} \pm 0.1^{\circ}$ ). The anode and freshly chloridised reference electrode were inserted, and the necessary connexions made. The cell was then evacuated and filled with hydrogen at an excess pressure of 100 mm. The rubber tube or the solution inlet was unplugged and hydrogen allowed to stream out while the solution storage flask was connected. (The outlet from this flask is narrow enough to fit inside the inlet to the cell so that entering solution does not touch the rubber.) The cell was then evacuated and solution allowed to enter. It was again filled with hydrogen and the storage flask removed and the inlet plugged. Bubbles of hydrogen in the side compartments were removed by running solution out of the exits and ground joints. The cathode compartment was filled with mercury to just above the bottom of the dropper, and a turn of the dropper-bubbler tap, followed by evacuation of the cell, caused the bubbling process to occur. A suitable potential (about 1 volt) was then applied to the pool of mercury and electrolysis continued until a potential of 0.6 volt gave  $10^{-8}$  amp. or less on a stationary surface. The current during bubbling was still above  $5 \times 10^{-7}$ . This state was reached in  $\frac{1}{2}$ –3 hours. The rubber tube supplying hydrogen to the bubbler was then pinched and hydrogen admitted to the cell by the side-tube. When the mercury had risen above the dropper-bubbler tap the latter was closed. The remaining mercury was sucked out of the

cathode compartment into the waste until the meniscus was below the graduated portion of the exit. The solution exits in the side compartments were opened momentarily to allow purified solution to run through the diaphragms, and thus prevent further the diffusion of impurities into the cathode compartments. The cathode lead was changed over to the dropper, the latter turned on, and measurements started.

To take a reading the dropping-rate was adjusted to about 2 drops per sec. and allowed a few minutes to become steady. The potentiometer was adjusted to the desired value, the applied potential was brought up to this by means of the sliding resistances, and the current was read. The dropped-mercury was sucked to the bottom of the graduated tube, and the time and number of drops required to fill a certain number of graduations were noted. The current was then read again, and if it had altered (through change in dropping-rate) the process was repeated, or, if the alteration was small the mean was taken. The potentiometer was then adjusted to a new potential and all the above measurements repeated. The whole range of potential was traversed rapidly at first and in detail later. Thus any general drift with time could be detected, but was never found in well-purified solutions. After a "run" the solution was blown out of the cell and fresh solution introduced. At least two "runs" were done at each concentration. At each change of concentration the cell was well rinsed with the new solution without dismantling, and a freshly chloridized reference electrode was introduced. Whenever a new substance was used the cell was dismantled and cleaned.

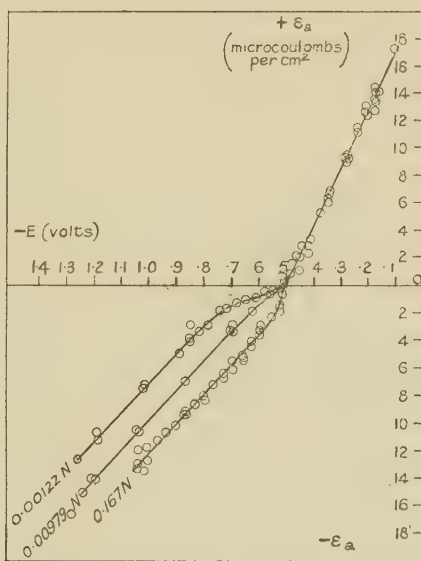
### *Results.*

Measurements of  $\epsilon$  were made in hydrochloric acid of molar concentration 0.1, 0.01, 0.0001, 0.00005, and in sodium chloride of concentration 0.1, 0.002, 0.0002. In the most dilute solution of each substance the resistance of the electrolyte in the cathode compartment affected the measured potential, so the only significant results obtained in these two solutions were the potentials for the zero  $\epsilon$  (*i. e.*, the electrokinetic potentials), which are independent of the resistance of the solution. In the other solutions the dilution caused no difficulties except that for some reason the negative half of the curve for 0.002 N sodium chloride could not be measured.

The values of  $\epsilon$  are shown plotted against  $E$  (the potential referred to silver-silver chloride in the same solution) in figs. 4-6. Fig. 6 shows inset the effect of using different

dropping-rates and degrees of purification, and the method of correcting for I. Fig. 4 shows the effect of concentration in the case of hydrochloric acid (uncorrected, as the method of correcting had not yet been developed). Results were obtained with three different dropping electrodes: the first, in which mercury ran down an amalgamated platinum wire, was used in a preliminary run with a different type of cell, and gave a value for " $K_+$ " (see Table I. on p. 789), agreeing closely with those obtained with the two "inverted cup" electrodes in the final cell.

Fig. 4.

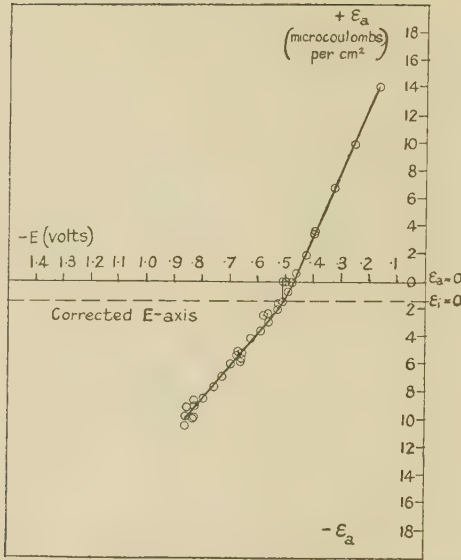


Capacity per cm.<sup>2</sup> (at constant potential) of a mercury electrode, measured in hydrochloric acid at different concentrations.

Table I. gives values derived from the graphs, which are used in the subsequent discussion. They are  $E_0$ ,  $E_+$ , and  $E_-$  (the values of  $E$  for  $\epsilon=0$ ,  $-10$ , and  $+10$  respectively), and  $K_+$  and  $K_-$  (the slopes of the lines when  $q=-10$  and  $+10$  respectively). The  $K$  values are given in microfarads per cm.<sup>2</sup>, and the  $E$  values in volts.

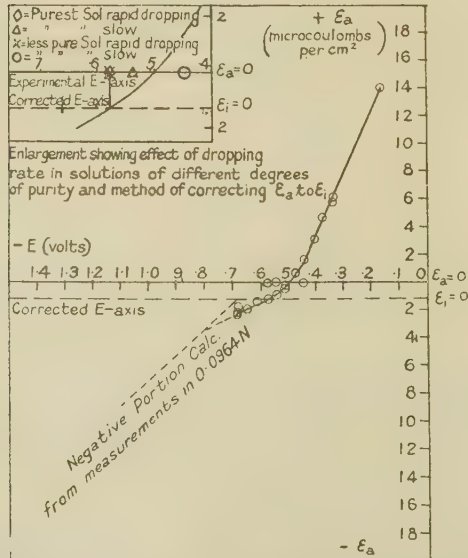
The agreement of  $K_+$  for hydrochloric acid and sodium chloride is unexpected, since  $K_+$  is supposed to depend on the radius of the positive ion.  $K_-$ , on the other hand, which is supposed to depend on the negative ion (chloride in both

Fig. 5.



Capacity per cm.<sup>2</sup> of a mercury electrode, measured in 0.0964 N. sodium chloride.

Fig. 6.



Capacity per cm.<sup>2</sup> of a mercury electrode, measured in 0.00185 N. sodium chloride.

TABLE I.

O.	I. Graph. Substance.	II. Con- centration.	III. K +	IV. K -	V. $-E_0$		VI. $-E_+$		VII. $-(E_+ - 0.11 \log c)$		VIII. $-E_-$	
					A. uncorr.	B. corr.	A. uncorr.	B. corr.	A. uncorr.	B. corr.	A. uncorr.	B. corr.
—	HCl	0.1613†	21.5	—	0.425	—	.866	—	.772	—	—	—
4	"	0.1613	22.0	43.4	0.464	—	.856	—	.762	—	.240	—
4	"	0.00980	21.8	44.7	0.510	—	.964	—	.736	—	.250	—
4 and 7	"	0.00122	21.6	45.1	0.578	—	1.109	—	.774	—	.259	—
—	"	0.00004	—	—	0.578	—	—	—	—	—	—	—
5	NaCl	0.0964	21.8	48.8	0.475	0.512	.859	.929	.739	.809	.262	.293
6	"	0.00185	—	47.6	0.498	0.575	—	(1.171)*	—	—	.252	.279
—	"	0.000168	—	—	0.476	0.529	—	(1.295)*	—	—	—	(.279)*
					(Const.).		(Const.).		(Const.).		(Const.).	

† Using another type of dropper and cell.

\* Calc. from measurements at higher concentrations.



cases), shows a slight change. The two series were done with different dropping electrodes, which may have caused this apparent reversal of the expected behaviour, but the discrepancy between the two chloride-ion values is not nearly as big as the difference in radius of the hydrogen and sodium ions. It might be thought that  $K_+$  is due to the hydrogen ion in both cases; but this is discounted by the positions of the linear regions along the E axis.

#### COMPARISON OF THEORY AND EXPERIMENT.

The following tests show that Stern's theory gives a truer picture of the electrolytic double layer than any other, and that under the conditions of these measurements  $\eta_0$  and  $\epsilon_i$  are probably identical:—

(1) The Helmholtz theory gives  $\eta_0$ =a linear function of  $\Psi_0$  at all potentials.

The Chapman-Gouy theory gives  $\eta_0$ =an exponential function of  $\psi_0$  at all potentials.

Stern's theory gives  $\eta_0$ =an exponential function of  $\psi_0$  when  $\psi_0$  and C are small, and a linear function when they are large. A glance at the series of experimental curves shows that Stern's theory is the only one which can fit them.

(2) Stern's theory gives that if  $\psi_0$  is large,  $\psi_0$  for a given value of  $\eta_0 = \text{const.} - RT/F \log C$  if  $\eta_0$  is positive,  
or  $= \text{const.} + RT/F \log C$  if  $\eta_0$  is negative.  
Hence, for a given value of  $\eta_0$ ,  $E = \text{const.}$  independent of C, if  $\eta_0$  is positive, and  $(E - 2 RT/F \log C) = \text{const.}$  if  $\eta_0$  is negative (since  $\psi_R = \text{const.} - \frac{RT}{F} \log C$ ).

The quantities  $E_-$  and  $(E_+ - 2RT/F \log C)$  in Table I.\* should therefore be constant, and so they are, within the limits of error. The series of graphs in fig. 4 shows clearly the shift of the negative portion of the curve along the axis with dilution, while the positive portion is stationary.

(3) The theoretical curve for  $C=0.001$  has been evaluated, using the values of  $K_0$  and  $\psi_R$ , obtained as described below, and neglecting  $\phi_+$  and  $\phi_-$ . It is plotted beside the experimental curve in fig. 7, and the correspondence is striking.

(The slopes of the straight portions are experimental, not theoretical, as they depend on  $K_0$ , and by adjusting  $\phi_+$  and  $\phi_-$  they can be moved along the axis till they coincide with the experimental curve.)

\*  $E_-$  corresponds to an excess of negative ions on the solution side, and so to a positive value of  $\eta_0$ .

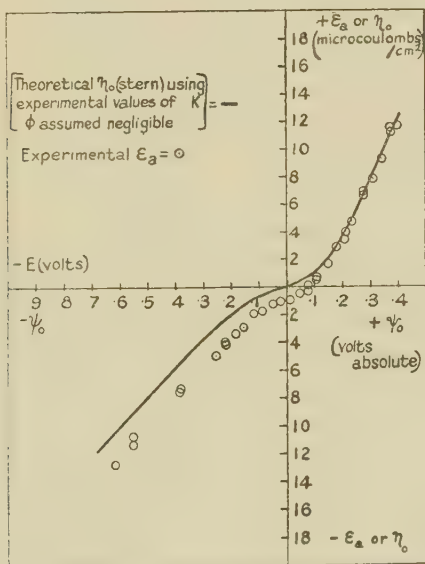
The features (1) and (2) above were noticed in the experimental curves independently of Stern's theory, which was only studied after the results in hydrochloric acid had been obtained.

# CALCULATION OF $K_0$ , $\psi_R$ , $\phi_+$ AND $\phi_-$ , FROM THE EXPERIMENTAL CURVES, USING STERN'S EQUATION.

## Calculation of $K_0$ .

$K_0$ , the capacity per  $\text{cm}^2$  of the adsorbed portion of the double layer, is the limiting slope of the curve of  $\eta_0$  against

Fig. 7.



Comparison of theoretical and experimental curves for electrolytic double layer in 0.00122 N hydrochloric acid.

$\psi_0$  at very high potentials. Such potentials are nearly but not quite obtainable in practice, so a small correction must be applied to the measured value of  $\frac{d\eta_0}{d\psi_0}$ , called  $K$ , as follows:—

From equation (3) above

$$K_0 = \frac{K}{1 - \frac{K}{d\eta_0/d\psi_1}} \dots \dots \dots (4)$$

From equations (2  $b_+$ ) and (1  $b_-$ ),

$$\frac{d\eta_+}{d\psi_1} = \frac{-F}{RT} (\eta_+ - \frac{1}{2}\eta_{2+}),$$

$$\frac{d\eta_-}{d\psi_1} = \frac{F}{RT} (\eta_- - \frac{1}{2}\eta_{2-}),$$

where  $\eta_{2+}$  and  $\eta_{2-}$  = charge in diffuse layer due to positive and negative ions,  $= -\frac{B\sqrt{c}}{x}$  and  $+B\sqrt{c}x$  respectively. Taking values of  $\eta_0$  large enough to be equal to  $\eta_+$  or  $\eta_-$ , and substituting  $\frac{d\eta_+}{d\psi_1}$  and  $\frac{d\eta_-}{d\psi_1}$  for  $\frac{d\eta_0}{d\psi_1}$  in equation (4),

$$K_{0+} = \frac{K_+}{1 + \frac{K_+ RT}{F(\eta_+ - \frac{1}{2}\eta_{2+})}},$$

$$K_{0-} = \frac{K_-}{1 - \frac{K_- RT}{F(\eta_- - \frac{1}{2}\eta_{2-})}},$$

where  $K_+$  is the experimental slope when  $\eta_0$  is large and negative (see footnote on p. 790),  $K_-$  is the experimental slope when  $\eta_0$  is large and positive and  $K_{0+}$  and  $K_{0-}$  are the capacities of the adsorbed layer when composed solely of positive or solely of negative ions. When  $\eta_0$  is large the term involving it is small and  $\frac{\eta_0}{\eta_2}$  is large. Therefore,  $\eta_2$

need only be estimated approximately from the simple theoretical curve, ignoring  $\phi_+$  and  $\phi_-$ . If the experimental data justified great accuracy  $\eta_2$  could be obtained more exactly by successive approximation after calculating the other quantities.

From the values in Table I. of  $K_+$  and  $K_-$  for the most dilute solutions in which they were successfully measured (where the above approximations are best justified) the following values of  $K_0$  were found:—

Table II.

For hydrochloric acid	$K_{0+} = 23.3 \pm 0.5$	microfarads per cm. <sup>2</sup> .
	$K_{0-} = 53.7 \pm 1.7$	“ “ “
For sodiumchloride	$K_{0+} = 23.6$	“ “ “
	$K_{0-} = 57.3 \pm 1.4$	“ “ “

(The limits of error given represent the maximum variation in the measurements of  $K$  at all concentrations.)

Stern calculated from the electrocapillary measurements of Krüger and Krumreich<sup>(4)</sup> in  $\text{KNO}_3$ ,  $K_0=29$  for both ions.

A check on the above calculation is provided by the fact that the theoretical curve for hydrochloric acid using these values of  $K_0$ , which is given in fig. 7, runs parallel to the experimental one at  $\eta_0=+10$  and  $-10$ , while when  $K$  is used instead of  $K_0$  the lack of parallelism is quite apparent.

*The values of  $\psi_R$ ,  $\zeta$ ,  $\phi_+$ , and  $\phi_-$ .*

$\psi_R$ , the absolute\* electrical potential of the reference electrode, is nearly equal, at low concentrations, to  $-E_0$ , the electrokinetic potential relative to the reference electrode. The two quantities differ by  $\zeta$ , the absolute value of the electrokinetic potential. If Stern's equation is assumed to be correct,  $\zeta$  can be calculated from the experimental curves, and is found to be of the order  $-0.003$  volt in  $\text{N}/500$  sodium chloride. The same calculation yields values for the specific absorption potentials  $\phi_+$  and  $\phi_-$  of the order of  $-0.02$  volt for the hydrogen, sodium, and chloride ions. The calculation depends very much on exact values of  $E_0$ , which the present apparatus was not specially designed to give, so the above figures are only provisional. A similarly provisional value of  $+0.47 \pm 0.03$  volt can be given for the absolute potential  $\psi_R$  of the silver-silver chloride electrode in decinormal sodium chloride. The theoretical significance of this quantity, and its relation to results of other workers (*e. g.*, Bennewitz and Schulz<sup>(6)</sup>, Billiter<sup>(9)</sup>, Bodforss<sup>(10)</sup>), will be discussed in a later paper.

*Calculation of  $\eta_0$  for the sodium amalgam electrode at its equilibrium potential.*—An approximate calculation from the experimental curves shows that if  $a$  is the activity of sodium in an amalgam, taking that in a 0.1 per cent. amalgam as unity, then

$$\eta_0 = -37.1 + 1.29 \log a \pm 1.5 \text{ microcoulombs per cm.}^2$$

at the equilibrium potential in sodium chloride of any concentration. The assumption is made that the electrolytic double layer on sodium amalgam is arranged as on mercury if the solution is sodium chloride in both cases.

\* In this paragraph potentials arising from a possible orientation of solvent dipoles are neglected.

## SUMMARY OF NUMERICALLY DETERMINED CONSTANTS.

1. The capacity of the adsorbed layer when consisting of only one kind of ion is—

For the hydrogen ion  $23.3 \pm 0.5$  mfd. per cm.<sup>2</sup>.

„ „ sodium ion 23.6

„ „ chloride ion  $53.7 \pm 1.7$  „ „ „ (measured in HCl).

or  $57.3 \pm 1.4$  „ „ „ (measured in NaCl).

2. The specific adsorption potentials of the hydrogen, sodium, and chloride ions are probably negative and of the order 0.02 volt.

3. The “absolute” electrokinetic potential of mercury in N/500 sodium chloride is probably negative and of the order 0.003 volt.

4. The “absolute” potential of the silver-silver chloride electrode in decinormal sodium chloride is  $+0.47 \pm 0.03$  volt.

5. The charge in the double layer of a sodium amalgam electrode in equilibrium with a solution of sodium chloride of any concentration is

$$-37.1 + 1.29 \log a \pm 1.5 \text{ microcoulombs per cm.}^2$$

where  $a$  is the activity of sodium in the amalgam, taking that in a 0.1 per cent. amalgam as unity.

## SUMMARY.

1. The “capacity per cm.<sup>2</sup> at constant potential” of the electrolytic double layer on mercury has been measured in hydrochloric acid and sodium chloride, over a wide range of concentration and potential.

2. The results show good agreement with the theoretical equation of Stern.

3. Stern's equation has been used to calculate various quantities from the experimental data.

I wish to express my sincere thanks to Sir Harold Hartley, F.R.S., to Mr. O. Gatty, and to others, for helpful advice and criticism throughout the course of this work.

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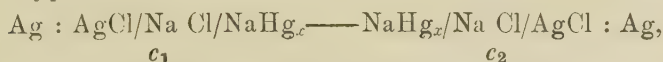


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LXXIII. *The Problem of the Sodium Amalgam Electrode in Dilute Solutions.* By J. ST. L. PHILPOT, B.A., N. L. ROSS-KANE, B.A., B.Sc., and J. H. WOLFENDEN, M.A., *Fellow of Exeter College, Oxford* \*.

IN the determination of the activity of an electrolyte by measurements of the E.M.F. of a cell with electrodes reversible to cation and anion respectively, it is well known that a self-contained determination is only possible if measurements are extended into the range of concentration in which the limiting equation of Debye and Hückel holds. This condition must always be fulfilled if an unequivocal linear extrapolation to determine  $E^\circ$  is to be made. The extent of the limiting range of concentration is not well defined, but for strong uni-univalent electrolytes its upper limit is about 0.01 N in water and 0.002 N in methyl alcohol, and diminishes with the dielectric constant of the solvent.

Precision in E.M.F. measurement becomes progressively more difficult as the dilution of the electrolyte increases, and in the case of amalgam electrodes the disturbing effects at high dilution take a particularly aggravated form. Comparatively few workers have extended their measurements with alkaline amalgam electrodes below N/100, and their measurements have usually been made with double cells of the type



in which the disturbing effects at the two intermediate amalgam electrodes cancel one another to an unknown extent.

Wolfenden, Wright, Ross-Kane, and Buckley<sup>(1)</sup> showed that the E.M.F. of the cell



\* Communicated by Sir Harold Hartley, F.R.S.

falls off rapidly from the true equilibrium value below a concentration of  $\cdot 005$  N. This leaves no intermediate range of concentration free from both the complex interionic effects at high concentration and the disturbing electrode effects at low concentration, and therefore yields no results susceptible to linear extrapolation. A recent paper by Scatchard and Tefft<sup>(2)</sup> describes the anomalous behaviour of the calcium amalgam electrode and stresses the complexity of the problem.

The experiments described in the present paper refer to the sodium amalgam electrode in aqueous solution and were undertaken in the hope of throwing some light on the nature of the disturbing effects at high dilution and on the conditions under which they are likely to be insignificant. In particular we wished to examine the influence on the potential of the amalgam electrode of such factors as the form of electrode, the rate of amalgam flow, and the presence of reducible impurities in the solution.

After an account of the experimental results a mechanism of the electrode processes is suggested and is applied to interpret the results obtained, and finally the conditions most favourable to precise measurement are discussed.

### *Experimental.*

The E.M.F. of the cell



was measured with sodium chloride solutions ranging in concentration from normal to  $0\cdot 0001$  N, the amalgam concentration being varied from  $0\cdot 3$  per cent. to  $0\cdot 005$  per cent. by weight. Each cell consisted of a single compartment containing the amalgam and silver-silver chloride electrodes, connected by thick rubber tubing to a container for waste amalgam (see fig. 1); the cells were immersed in a paraffin thermostat at  $25^\circ \pm 0\cdot 1^\circ$ . To save time three cells were used simultaneously, the three amalgam electrodes being supplied from the same reservoir. Of these three electrodes one was a fine capillary dropping electrode, another was a capillary dropping electrode of wider bore, while the third consisted of an overflowing capillary electrode.

The solutions were made up from water distilled in a stream of nitrogen and condensed on tin. Before the introduction of solution into flasks or cells, the air was displaced from the latter by a stream of nitrogen.

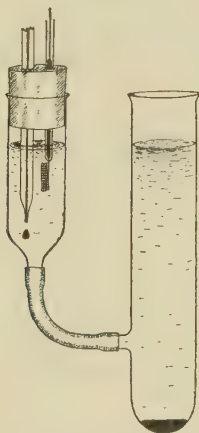
A continuous flow of solution past the electrodes was

dispensed with in these measurements, since interest was focussed primarily on the amalgam electrode itself.

The E.M.F. of each cell was measured over a range of dropping-rates from 1 drop per second to that giving a continuous column of amalgam 1 cm. in length. Measurements were continued for about an hour, when a rapid fall of E.M.F. began, which indicated alteration in composition of the solution. The effect of dissolved oxygen was occasionally studied by bubbling the gas through the solution.

A few later experiments were made with the cell described in the accompanying paper on the electrolytic double layer<sup>(3)</sup>.

Fig. 1.



One of the triplet cells.

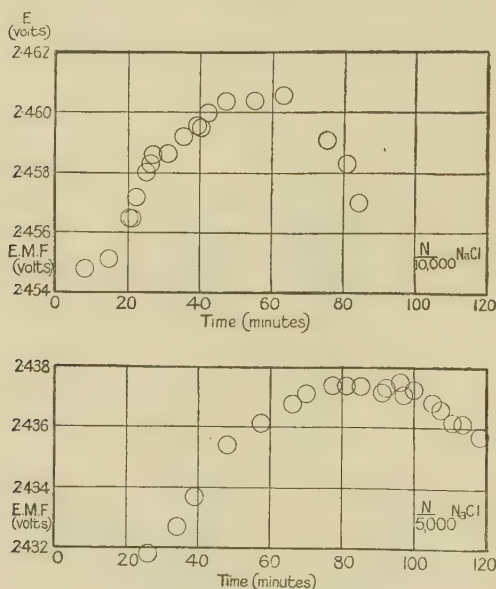
The solution could be purified electrolytically from reducible impurities down to a molar concentration of  $10^{-9}$  before turning on the amalgam. Alternatively the cell could be emptied and rapidly refilled from a storage flask with solution containing  $10^{-7}$  gram-equivalents per litre of reducible impurity, while the amalgam was dropping steadily; this was equivalent to using flowing solution. The instantaneous potential at any stage of drop formation or immediately after switching off a small current was measured on a few occasions with a capillary electrometer of the Keith-Lucas type used in physiological work. For these later experiments an over-flowing electrode was used exclusively.

*Results.*

From the work as a whole the following empirical generalizations may be made :—

(1) In stationary solutions containing a considerable quantity of reducible impurity, such as were used for all the earlier experiments, the E.M.F. rises rapidly at first, stays constant for a time, and then falls rapidly. The height of the initial rise increases, and the length of the period of

Fig. 2



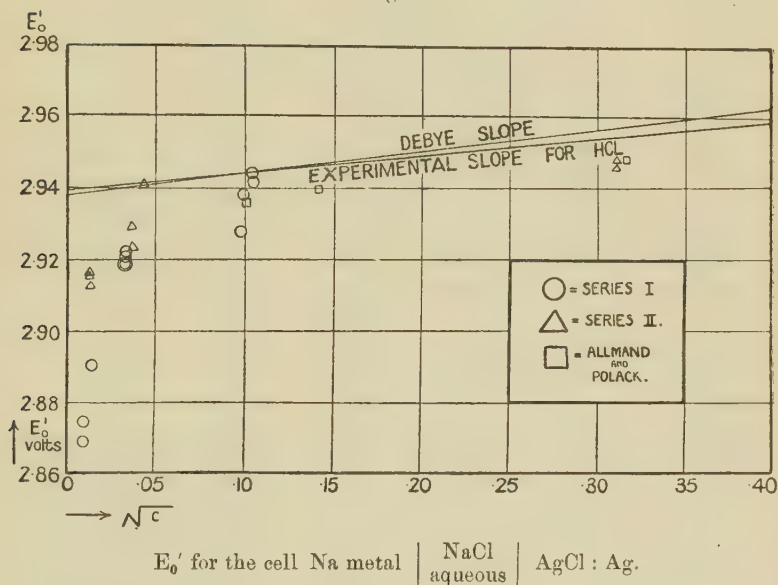
Variation of E.M.F. with time.

constancy decreases, with decrease in concentration of sodium chloride. The initial rise was not observed in the few experiments with solutions containing  $10^{-7}$  to  $10^{-9}$  gram-equivalents per litre of reducible impurity, but it is premature to say that it does not occur in them. The graphs of the E.M.F. plotted against time (fig. 2) show the effect in question.

(2) In water, as in methyl alcohol, the deviation from the true equilibrium E.M.F. begins to occur above the range of concentration in which the logarithm of the activity coefficient is a linear function of  $\sqrt{c}$ , so that the necessary

extrapolation of  $E_0'$  to  $c=0$  cannot be carried out. This was shown by plotting the function " $E_0'$ " against the square root of the concentration. To calculate  $E_0'^{(4)}$  the maximum E.M.F. of the overflowing electrode cell was first corrected to give the E.M.F. relative to sodium metal by graphic interpolation from the combined data of Lewis and Kraus<sup>(5)</sup> and Richards and Conant<sup>(6)</sup>. By subtracting  $\frac{2RT}{F} \ln c$  from this corrected E.M.F., the function  $E_0'$  i

Fig. 3.



obtained whose limiting value at infinite dilution represents the E.M.F. of the cell:—

Na metal/aqueous NaCl of unit activity/AgCl : Ag.

The curve obtained by plotting  $E_0'$  against  $\sqrt{c}$  is everywhere concave to the concentration axis. Fig. 3 gives these values, together with lines showing the Debye-Hückel limiting slope and that observed for hydrochloric acid by Nonhebel and Hartley<sup>(7)</sup>, both drawn through our experimental value for  $c=0.01$  N. The results of Allmand and Polack<sup>(8)</sup>, recalculated to a common basis, are given in the range where they overlap. The Table gives the numerical values.



(3) At concentrations of 0.001 N and 0.0002 N solutions containing  $10^{-7}$  to  $10^{-9}$  gram-equivalents/litre of reducible impurity have an E.M.F. a few millivolts higher than the less carefully purified solutions used at first; but this higher

Concentration of solution in mols per litre, c.	$\sqrt{c}$ .	Amalgam concentration in grams per cent.	Observed E.M.F.	$E_0'$ referred to metal.	
0.00011	0.0105	0.0734	2.4513	2.8747	<i>Series I.</i> Triplet cells as described in text; solutions freed from reducible impurities.
"	"	"	2.4558	2.8692	
0.00021	0.0145	0.0739	2.4445	2.8909	
0.00107	0.0327	0.0246	2.3563	2.9185	
0.00108	0.0329	0.3060	2.4399	2.9184	
0.00109	0.0330	0.0471	2.3774	2.9223	
"	"	"	2.3756	2.9205	
0.00957	0.0978	0.3000	2.3377	2.9282	
0.00989	0.0994	0.0246	2.2617	2.9381	
0.0110	0.1049	0.0471	2.2780	2.9417	
"	"	"	2.2809	2.9446	
0.9801	0.9900	0.0233	2.0418	2.9557	
0.9972	0.9985	0.3000	2.1293	2.9586	
0.000168	0.0139	0.0550	2.4692	2.9129	<i>Series II.</i> Cell as described in previous paper; solutions purified down to $10^{-7}$ or $10^{-9}$ gram-equivalents of reducible impurity per litre.
"	"	"	2.4722	2.9159	
"	"	0.1320	2.5011	2.9164	
0.00133	0.0365	"	2.4009	2.9232	
"	"	"	2.4073	2.9296	
0.00185	0.0430	0.0550	2.3737	2.9408	
0.0964	0.3105	"	2.1782	2.9485	
"	"	0.0058	2.1156	2.9463	
0.100	0.3162	0.1389	(Calomel used as reference electrode.)	2.9486	Allmand and Polack's results.
0.0200	0.1414	"		2.9399	
0.0100	0.1000	"		2.9361	

E.M.F. is still well below the probable equilibrium value inferred from the Debye-Hückel slope and from the experimental  $E_0'$  curve for hydrochloric acid in aqueous solution.

4. In 0.001 N solutions, with dropping-rates down to 0.5 per sec., the instantaneous potential during drop formation, as measured with the capillary electrometer, is lowest

when a drop has just fallen leaving a fresh surface ; it rises rapidly by about 20 mv. to a value which remains constant during the rest of the life of the drop.

(5) When a current of  $10^{-5}$  amps. is passed in 0.0001 N solution containing  $10^{-7}$  gram-equivalents per litre of reducible impurity, the potential immediately after switching off the current is about 1 mv. higher than normal, and persists for the whole life of the drop.

(6) The agreement between the values of  $E_0'$  calculated from measurements of E.M.F. made with the same sodium chloride solution but with amalgam electrodes of widely different concentration is fairly satisfactory.

(7) The comparison of a silver-silver chloride electrode in the presence of a trace of alkali with a similar electrode in neutral solution showed that the alkali produced by the amalgam in a stationary solution might have a considerable effect on the reference electrode. The following are typical results, the electrode in neutral solution being negative :—

Concentration of NaCl ...	0.01	0.001	0.0001
Change in potential due to 0.00017 N :			
NaOH .....	0.3 mv.	30 mv.	60 mv.

(8) The overflowing electrode gives a far steadier E.M.F. than either a coarse or a fine dropping electrode, though the last often gives a higher value by as much as 2 mv.

(9) The variation of E.M.F. with dropping-rate was scarcely detectable, and the small effect (ca. 0.1 mv.) was irregular in sign. Below 2 drops per sec. readings became erratic in the earlier experiments, but in the later ones steady readings were obtained down to 0.4 drops per sec. This is probably connected with the fact that in the later experiments the bore of the electrode increased towards the orifice so that there was no tendency for the amalgam column to retreat from the end under the influence of surface tension. With this type of electrode the slowest dropping-rate gave the highest E.M.F.

(10) When oxygen was bubbled through the cell the E.M.F. fell rapidly and continued falling for a short time after the bubbling was stopped. Bubbling for 5 minutes lowered the E.M.F. by 1 mv. in N solution, and 8 mv. in N/100.

*Discussion.*

The electrode process may be described in the following manner :—When a fresh drop of amalgam is formed, sodium ions enter the electrolytic double layer from the amalgam and continue to do so till the potential is sufficient to maintain equilibrium. At this potential, however, two constituents of the solution are not in equilibrium—reducible impurities and hydrogen ions. The former are reduced at a rate proportional to their concentration, if small, and independent of potential, while the latter are reduced to hydrogen at a rate determined by one of the two equations for over-voltage <sup>(9)</sup>. The current required for these processes must be supplied by sodium ions passing from the double layer into the solution and being replaced from the amalgam. If some part of this compensating process goes too slowly the E.M.F. will fall below the equilibrium value. The shape of the curve of  $E_0'$  against  $c$  (fig. 3) can be explained on the assumption that the departure of the E.M.F. from equilibrium which is required to produce the compensating current increases to appreciable values at low concentrations.

The formation of the double layer requires quite a large quantity of sodium ions which is calculated in the accompanying paper <sup>(3)</sup> and is equivalent to  $-34$  microcoulombs per sq. cm. The capillary electrometer measurements showed that this double layer is not formed instantaneously, and the low potential during its formation must contribute to the mean potential as ordinarily measured to an increasing extent as the dropping-rate is increased. This sets an upper limit to the permissible dropping-rate. A lower limit is set by the reduction processes described above, for if the sodium, which must dissolve in compensation during the life-time of a drop, exceeds a certain quantity per cm.<sup>2</sup> surface, then the thickness of the amalgam layer supplying it is such that the process of diffusion becomes too slow, quite apart from the effects in the solution described below. The same consideration of diffusion also sets a limit to the permissible dilution of the amalgam.

So much for occurrences in the amalgam. The adjacent layer of solution is probably even more prominent in determining the measured E.M.F. In the fraction of a second which is the life of a drop not much diffusion or mixing can occur. There will, therefore, be rapid changes, confined to a thin layer near the electrode surface and little affected by flowing solution, as well as the slow steady changes in the bulk of the solution if stationary. The changes consist in

(a) diminution of concentrations of hydrion and reducible impurities, which raises the E.M.F. by allowing nearer approach to equilibrium in the double layer, and (b) increase in concentration of sodium ion, which lowers the E.M.F., according to Nernst's equation. (Since  $dE/dc \propto 1/c$  this effect is very prominent at low concentrations.) As the process continues therefore the E.M.F. will tend first to rise towards the equilibrium value as hydrion and impurities disappear, and then to fall off as sodium ion accumulates. Consideration of the solution as a whole in this way provides the simplest explanation of the shape of the E.M.F.-time curves shown in figs. 1 and 2 and described in section 1. The same process should occur in miniature in the surface-film of solution during the life of each drop of amalgam, but so far only the initial rise has been observed even with a drop lasting 2 secs. (see section 4). Probably, however, if the capillary electrometer measurements were made with solutions more dilute than 0.001 N, both the initial rise and the final fall would be evident in the life of a single drop at the normal dropping rates. A contributing factor in the final fall must be the liquid junction potential due to the accumulation of hydroxyl ions round the amalgam electrode (see section 7). If the hydroxyl ion had a direct action on the silver-silver chloride equilibrium it would, on the other hand, raise the E.M.F. after the considerable time required for diffusion from the amalgam electrode. This has never been observed, but might have been masked by the final fall described above.

Most of the results have thus received a qualitative explanation:—

(1) The initial rise and final fall in the E.M.F. are due to removal of hydrion and reducible impurities and to accumulation of sodium ion respectively.

(2) The abnormally low E.M.F. in dilute solutions is due to the overlapping of all the factors described, in such a way that under no conditions can they all be absent as is possible in stronger solutions.

(3) The rate of reduction of impurities is independent of potential, while that of hydrion increases with it. Therefore with increasing dilution the lowering of E.M.F. will be due more to hydrion and less to impurities, and purification will be less effective in restoring the equilibrium value.

(4) The initial rise of the instantaneous potential of a fresh drop is due to the slowness of formation of the electrolytic double layer, either because of the slowness with which

sodium ions leave the amalgam, or because an abnormal number must leave it to compensate for the reduction processes. A final fall of potential of a long-lived drop should be observed under some conditions for reasons given above.

(5) Passage of a current compensates the reduction processes without dissolving sodium, so it should be possible in this way to separate the initial rise and the final fall at concentrations where they normally overlap. But it is impossible at present to tell how much current to pass, as the rate of reduction of hydrogen in neutral unbuffered solutions is extremely erratic, especially at these high potentials.

(6) It is impossible to calculate the influence of amalgam concentration without data as to the rates of dissolution of sodium from amalgams of various concentrations at various potentials, but the amalgam can certainly be too dilute, and it is possible that it may be too strong.

(7) Two ways have been suggested in which alkali can affect the reference silver-silver chloride electrode. Of these the liquid junction potential is believed to be the more important.

(8) The steadiness of the overflowing electrode is probably due to its greater mechanical stability. The higher E.M.F.s of the fine dropping one cannot be lightly dismissed, but have so far been unmeasurably erratic.

(9) Theoretically a very slow dropping-rate should give a low mean potential because of the predominance of the local "final fall," while a very high rate should give a low potential because of the predominance of the "initial rise," and intermediate rates should give a higher potential nearly independent of rate. It seems that the rates normally used are in this sense "intermediate" or slightly "high."

(10) When oxygen was bubbled through the solution it increased the reducible impurity, and the stirring brought up outlying portions of the solution which had not been reduced. Both these factors set back the "initial rise," *i. e.*, caused a fall of potential.

### *Conclusions.*

Our observations lead us to suggest that the following conditions are the most likely to lead to values approximating to the true equilibrium potential of the sodium amalgam electrode :—

(1) The use of an external current or of some equivalent



device is necessary if E.M.F. measurements are to be extended to concentrations below N/1000.

(2) Reducible impurities should not exceed  $10^{-7}$  gram-equivalents/litre. This requires carefully prepared water and rigid exclusion of air. Purification beyond this point is unnecessary.

(3) An intermittently renewed solution should be used in preference to a flowing one. The former will yield more information, and the latter will not necessarily give the highest E.M.F.

(4) The overflowing type of electrode is probably best. It should be of narrow bore throughout. If the dropping-rate is controlled with a tap the bore of the electrode must increase slightly towards the orifice. Dropping-rates down to 0.5 per sec. should be used if the amalgam is between 0.005 and 0.1 per cent.

(5) Although they require higher dropping-rates and rapid renewal of solution, concentrated amalgams are probably better than the dilute ones which have often been used.

#### *Summary.*

Measurements of electromotive force have been made with the sodium amalgam electrode in aqueous solutions of sodium chloride at high dilution. The nature of the various disturbing factors is discussed in the light of the phenomena observed and conditions likely to minimize their influence are suggested.

The authors desire to express their thanks to Sir Harold Hartley for his advice and encouragement throughout the work.

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LXXIV. *On Gibbs's Adsorption Equation for the Case of Binary Mixtures.* By R. K. SCHOFIELD, M.A., Ph.D., and E. K. RIDEAL, F.R.S.\*

IN recent years some confusion has arisen in the application of Gibbs's equation to binary mixtures. In developing a kinetic theory of surface films (Proc. Roy. Soc. A, cix. p. 57, 1925) the authors made use of the Gibbs equation

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \text{etc.},$$

for examining the nature of the surface phase of solutions. In the equation  $\sigma$  is the surface tension and  $\mu_1, \mu_2$ , etc., are the thermodynamic potentials of the independently variable components.  $\Gamma_1, \Gamma_2$ , etc., are the excess surface concentrations used in Gibbs's sense, namely: the number of moles of these components in excess per unit area of the interface, the excess being reckoned with respect to an imaginary geometrical surface which is parallel to, but not necessarily coincident with, the physical surface of discontinuity. Gibbs called this imaginary surface the "dividing surface."

The value of the individual terms on the right-hand side of the equation depends on the position chosen for the dividing surface, any one being made zero by a suitable choice; but their sum is independent of its position.

Use was made of this equation to analyze data for binary mixtures of ethyl alcohol and water. It was concluded, in the case of mixtures rich in alcohol, that the existence at the surface of a layer of closely packed alcohol molecules (which appears probable on other grounds) can only be conceded if at the same time it is supposed that a layer relatively rich in water exists below it.

Recently, W. F. K. Wynne-Jones † has put forward a treatment which, it is claimed, shows the existence of the close-packed alcohol layer without requiring the presence of the water-rich layer below it. In his paper, the essential importance of the imaginary "dividing surface" to the whole of Gibbs's theory is overlooked, the term "surface excess" being used without reference to this "dividing surface."

In the present case it is convenient to choose the position of the dividing surface, so that  $\Gamma$  for water is zero. To

\* Communicated by the Authors.

† Phil. Mag. clxi. p. 907 (1931).

make clear the method of fixing the dividing surface,  $D$ , let us imagine another surface,  $S$ , represented by the dotted line, to be described parallel to the physical surface but sufficiently far from it to be in the homogeneous liquid phase.  $D$  is so placed that the total quantity of water present in the system would be correctly computed by supposing the water concentration existing below  $S$  to continue unchanged to  $D$ , and there change abruptly to that obtaining in the vapour phase. If such an accumulation as we have suggested is present, the dividing surface will cut through the outermost layer of alcohol in somewhat the way indicated in the figure. To calculate  $\Gamma$  we must first calculate how much alcohol would be present if the alcohol concentration between  $S$  and  $D$  were the same as it is below  $S$ , and at  $D$  changed abruptly to the concentration in the vapour. This calculation would give an amount of alcohol less than that actually present, and the difference (reckoned per unit area of interface) is  $\Gamma$ . It should be clear from this that, with an accumulation of water molecules below the surface layer of alcohol,  $\Gamma$  will be less than the amount of alcohol in one square centimetre of the outermost layer. If, on the other hand, no such accumulation exists and the water and alcohol concentrations are uniform as far as the underside of the alcohol layer, then the dividing surface will be at  $D'$ , and  $\Gamma$  will be equal to the amount of alcohol in one square centimetre of the outermost layer. There appears to be no escape from this conclusion.

If, following Wynne-Jones, we assume that from 30 per cent. to 100 per cent. ethyl alcohol the surface is covered by a layer of alcohol amounting to  $U = 8.2 \times 10^{-10}$  moles/cm.<sup>2</sup>, it is easy to calculate the excess of water immediately below this layer, since  $U - \Gamma$  is equal to the amount of alcohol which could be accommodated between  $D$  and  $D'$  if the concentration were the same as in the bulk. What we require is the amount of water that could be similarly accommodated, and this is evidently given by  $(U - \Gamma)R$ , where  $R$  is the ratio of water molecules to alcohol molecules in the bulk. Using the values of  $\Gamma$  calculated by Wynne-Jones from the vapour-pressure data of Dobson and the surface-tension data of Morgan and Neidle, we obtain the figures in the table and the curve, which give us a water adsorption falling to zero in pure alcohol and approaching one molecule of water to each of the adsorbed alcohol molecules in a mixture containing 60 per cent. of water.\*

No great accuracy can be claimed for these figures,\* as,

for one thing, they depend on the value chosen of  $U$ , the amount of alcohol in the surface layer, the very existence of which is only inferred from general considerations, and

Fig. 1.

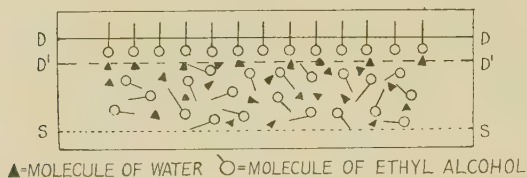
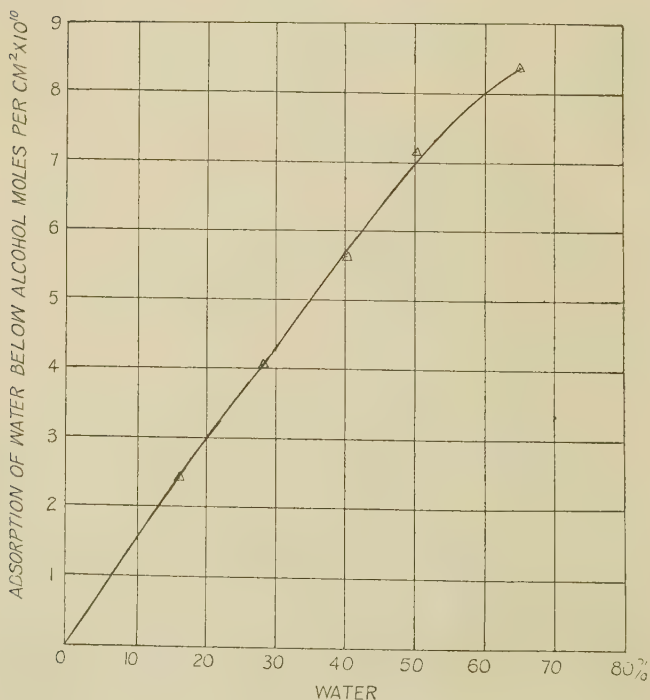


Fig. 2.



cannot be established from purely thermodynamic considerations. But any explanation involving the existence of this outermost layer must, to be thermodynamically consistent, also take account of the water accumulation.

Turning finally to the relation  $U = \Gamma + kc$  proposed by Wynne-Jones, it might be asked why  $c$  has been taken as the percentage by weight, rather than by volume or molecular volume. But such questions are really beside the point, seeing that the relation has no thermodynamic foundation and cannot, therefore, give results of any value.

### Summary.

The theory advanced by Wynne-Jones relating to the figures published by the authors for the adsorption of alcohol at the surface of alcohol-water mixture is criticized.

TABLE.

Per cent. Water.	Per cent. Ethyl Alcohol.	Ratio by weight $r$ .	Ratio by moles. $R$ ( $r \times 2.55$ ).	$\Gamma$ moles. per sq. cm. $\times 10^{10}$ .	( $U - \Gamma$ ) [ $U = 8.2$ ] $\times 10^{10}$ .	Adsorption of water below alcohol moles. per cm. <sup>2</sup> $\times 10^{10}$ .
65	35	1.86	4.74	6.45	1.75	8.3
50	50	1.0	2.55	5.4	2.8	7.1
40	60	0.666	1.70	4.9	3.3	5.6
28	72	0.389	0.99	4.2	4.0	4.0
16	84	0.191	0.487	3.3	4.9	2.4
0	100	0	0	0	0	0

The view originally advanced by the authors that the fall in the surface excess in strong alcohol solutions is due to the formation of a layer relatively rich in water below a closely packed surface-layer of alcohol is reasserted, and a calculation based on the experimental figures preferred by Wynne-Jones indicates that this accumulation of water rises from zero in pure alcohol to a value of the order of one water molecule to every adsorbed alcohol molecule in the neighbourhood of 60 per cent. water.

No theoretical foundation can be found for the relation  $U = \Gamma + kc$  proposed by Wynne-Jones.



LXXV. *Application of the Law of Photo-elastic Extinction to some Problems.* By J. KUNO, Assistant Professor of Civil Engineering, Kyushu Imperial University, Fukuoka \*.

[Plates XV. & XVI.]

I. *Introduction.*

THE law of photo-elastic extinction—that is, the principal stress difference at a point in a specimen multiplied by the thickness of the specimen is proportional to the order of extinction—has been obtained by the author with specimens of phenolite under simple stress†. In order to examine whether the law holds generally true at the point where both the principal stresses are not equal to zero it is attempted in the present paper to compare the values of stresses experimentally obtained by this law with the theoretical values in a roller and in a rectangular thick plate of two-dimensional stress.

II. *A Roller Diametrically Compressed.*

(1) *Theory.*

A number of mathematical solutions and photo-elastic experiments have been carried out for a roller diametrically compressed‡. The solution given in this article is somewhat different from others and will be compared with the photo-elastic test performed by using a specimen of phenolite.

We may take a system of curvilinear orthogonal coordinates  $\alpha, \beta$  defined by the equation

$$z = a e^{-\dots}$$

where

$$iz = x + iy, \quad w = \alpha + i\beta, \quad \alpha \geq 0, \quad \beta^2 \leq \pi^2.$$

Here the condition  $c = 0$  represents the circumference of a circle whose radius is  $a$ , and the condition  $\alpha = \infty$  its centre,

\* Communicated by the Author.

† Phil. Mag. xii. p. 503 (1931).

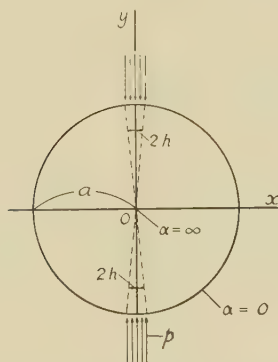
‡ Hertz, *Ges. Werk*, i. p. 285; Michell, Proc. London Math. Soc. xxxii. p. 35 (1900); Mesnager, *Ann. P. et Ch. Mém.* (71) iv. p. 160 (1901); Huber and Fuchs, *Phys. ZS.* xv. p. 298 (1914); König, *Ann. der Phys.* (4) lii. p. 553 (1917); Steinheil, *Diss. Giesen* (1920); Filon, Brit. Assoc. Report, Liverpool, p. 354 (1923); Föppl, *Drang und Zwang*, i. p. 320 (1924); Arakawa, Proc. Phys. Math. Soc. Japan, (3) vii. p. 174 (1925); Rirth, *Ann. der Phys.* (4) lxxix. p. 145 (1926); Tuzi, Scientific Papers, I. P. C. R. (Tokyo) viii. p. 251 (1928).

as shown in fig. 1. If we refer to such a system of coordinates, Prof. S. Yokota's general expression for stress-components in two-dimensional problems of elasticity\* becomes

$$\left. \begin{aligned} \widehat{\alpha}\alpha - \widehat{\beta}\beta - 2i\alpha\beta &= (1 - e^{-2i\beta})f_1'(w) - e^{\alpha - i\beta}f_2(w), \\ \widehat{\alpha}\alpha + \widehat{\beta}\beta &= \text{Real part of } 2f_1(w), \end{aligned} \right\} \quad (1)$$

where  $f_1(w)$  and  $f_2(w)$  are arbitrary functions of  $w$ . Let the load  $P$  be distributed on the area  $2hab$  with the uniform radial intensity  $p$ , where  $b$  is the length of the roller and  $2h$  is a small angle at the centre in radians intercepting the

Fig. 1.



loaded arc. Then the boundary conditions in the first quadrant must be

$$\left. \begin{aligned} [\widehat{\alpha\beta}]_{\alpha=0} &= 0, \\ [\widehat{\alpha\alpha}]_{\alpha=0} &= 0 \quad \text{for } (-\beta) < \left(\frac{\pi}{2} - h\right), \\ ,, &= -p \quad \text{for } (-\beta) > \left(\frac{\pi}{2} - h\right), \\ [\widehat{\alpha\alpha}]_{\alpha=0} &= -\frac{2p}{\pi} \left[ h + \sum_{n=1}^{\infty} (-1)^n \frac{1}{n} \sin 2nh \cos 2n\beta \right]. \end{aligned} \right\} \quad (2)$$

The boundary conditions in the other quadrants are naturally fulfilled from symmetry.

\* Journ. Soc. Mech. Eng. Japan, xxix. (April 1915).

Now put

$$\left. \begin{aligned} f_1(w) &= \frac{2p}{\pi} \sum_{n=0}^{\infty} A_{2n} e^{-2nw}, \\ f_2(w) &= \frac{2pa}{\pi} \sum_{n=0}^{\infty} B_{2n+1} e^{-(2n+1)w}. \end{aligned} \right\} \dots \dots (3)$$

Inserting (2) and (3) into (1), we find

$$A_0 = -h,$$

$$A_{2n} = (-1)^{n+1} \sin 2nh \quad \text{for } n > 0,$$

$$B_{2n+1} = 2nA_{2n} - 2(n+1)A_{2(n+1)}.$$

Then we have, finally,

$$\left. \begin{aligned} \widehat{\alpha\alpha} - \beta\beta - 2i\alpha\beta &= -\frac{4p}{\pi} (e^{2a} - 1) \sum_{n=1}^{\infty} (-1)^n e^{-2nw} \sin 2nh, \\ \widehat{\alpha\alpha} + \widehat{\beta\beta} &= -\frac{4p}{\pi} \left[ h + \sum_{n=1}^{\infty} (-1)^n \frac{1}{n} e^{-2na} \sin 2nh \cos 2n\beta \right]. \end{aligned} \right\} \dots \dots (4)$$

These equations enable us to obtain the stress-components at any point. In the circular domain excepting the circumference (4) can be transformed into

$$\widehat{\alpha\alpha} - \widehat{\beta\beta} = \frac{4p}{\pi D} (1 - e^{-2a}) \sin 2h [(1 + e^{-4a}) \cos 2\beta + 2e^{-2a} \cos 2h],$$

$$\begin{aligned} \widehat{\alpha\alpha} + \widehat{\beta\beta} &= \frac{2p}{\pi} \left[ \operatorname{arctg} \frac{\sin 2(h + \beta)}{e^{2a} + \cos 2(h + \beta)} \right. \\ &\quad \left. + \operatorname{arctg} \frac{\sin 2(h - \beta)}{e^{2a} + \cos 2(h - \beta)} - 2h \right], \end{aligned}$$

$$\widehat{\alpha\beta} = \frac{2p}{\pi D} (1 - e^{-2a}) (1 - e^{-4a}) \sin 2h \sin 2\beta,$$

where

$$\begin{aligned} D &= \{1 + e^{-4a} + 2e^{-2a} \cos 2h \cos 2\beta\}^2 \\ &\quad - \{2e^{-2a} \sin 2h \sin 2\beta\}^2. \end{aligned}$$

In the case where  $2h$  is very small we may put approximately

$$\begin{aligned} \sin 2h &= 2h, \quad \cos 2h = 1, \\ \operatorname{arctg} \left[ \frac{\sin 2h}{(e^{2a} + \cos 2h)} \right] &= \frac{2h}{(1 + e^{2a})}. \end{aligned}$$

Then we have on the horizontal and vertical diameters

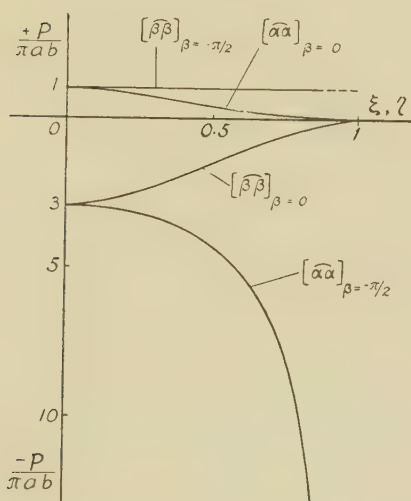
$$[\widehat{\alpha\alpha}]_{\beta=0} = \frac{P}{\pi ab} \left( \frac{1-\xi^2}{1+\xi^2} \right)^2,$$

$$[\widehat{\beta\beta}]_{\beta=0} = -\frac{P}{\pi ab} \left\{ \left( \frac{1-\xi^2}{1+\xi^2} \right)^2 - 1 \right\},$$

$$[\widehat{\alpha\alpha}]_{\beta=-\pi/2} = -\frac{P}{\pi ab} \frac{3+\eta^2}{1-\eta^2},$$

$$[\widehat{\beta\beta}]_{\beta=-\pi/2} = \frac{P}{\pi ab},$$

Fig. 2.



where  $\xi = x/a$  and  $\eta = y/a$ . The results of these calculations, plotted in fig. 2, show that they agree with the results given by Hertz and others under the assumption that each load acts at a point. As a measure of the accuracy of the above reduction we have the total pressure on the horizontal diameter as follows :

$$2 \int_0^a b [\widehat{\beta\beta}]_{\beta=0} dx = -P.$$

Let  $\gamma$  be the angle which the normal at  $(\alpha, \beta)$  to the line of the  $\alpha$ -family that passes through this point makes with

the axis of  $x$ , and  $\theta$  be the angle which a principal axis at  $(\alpha, \beta)$  makes with the axis of  $x$ . Then we have generally

$$2(\gamma - \theta) = \text{Amplitude of } (\widehat{\alpha\alpha} - \widehat{\beta\beta} - 2i\widehat{\alpha\beta})^*.$$

In the present case it becomes

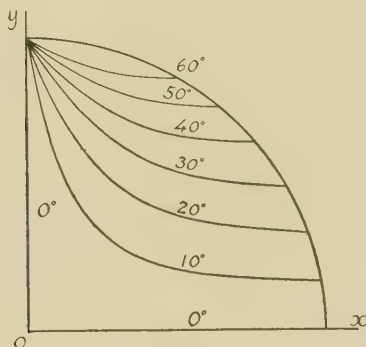
$$\operatorname{tg} 2(\theta + \beta) = \frac{(1 - e^{-4\alpha}) \sin 2\beta}{(1 + e^{-4\alpha}) \cos 2\beta + 2e^{-2\alpha} \cos 2h}$$

which may be shown to be transformed into

$$y^2 - x^2 + 2xy \cot \theta = a^2$$

provided that  $\cos 2h = 1$ . Turn the axes through an angle

Fig. 3.



$(\theta/2 - \pi/4)$ , the origin remaining the same. Referring to the new axes we get

$$Y^2 - X^2 = a^2 \sin \theta.$$

This equation represents the isoclinic lines,  $\theta$  being a parameter. Such lines are shown in fig. 3 for one quadrant of the section, the others being deducible from symmetry.

Next, denoting the difference of the two principal stresses at a point by  $S$ , we have generally

$$S^2 = \{\widehat{\alpha\alpha} - \widehat{\beta\beta}\}^2 + \{2\widehat{\alpha\beta}\}^2 +$$

In the present case we have

$$S = 4p(1 - e^{-2\alpha}) \sin 2h / \pi D^{1/2}, \quad . \quad . \quad (5)$$

\* Tech. Rep. Kyushu Imp. University, v. p. 265 (Feb. 1931)

† Loc. cit.



where  $p$  may be expressed in the form  $p = P/2hab$ . If we insert the law of photo-elastic extinction  $Sd = nK$  into (5), and put approximately

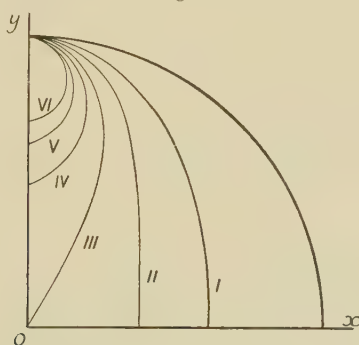
$$D^{1/2} = 1 + e^{-4a} + 2e^{-2a} \cos 2\beta \quad \text{and} \quad \sin 2h = 2h,$$

we have

$$n = \frac{4P}{\pi a K} \frac{1 - e^{-2a}}{1 + e^{-4a} + 2e^{-2a} \cos 2\beta}$$

where  $n$  is the order of extinction and  $K$  is the coefficient of photo-elastic extinction. Fig. 4 shows the isochromatic

Fig. 4.



lines calculated from the above equation for the case  $\frac{4P}{\pi a K} = 3$ . On the axis of  $y$  the equation (5) becomes

$$S = \frac{4p \sin 2h}{\pi} \frac{1 - \eta^2}{1 + \eta^4 - 2\eta^2 \cos 2h},$$

where  $\eta = y/a$ . Differentiating  $S$  with respect to  $\eta$ , and equating the result to zero, we get a special value of  $\eta$  given by

$$\begin{aligned} \eta_0^2 &= 1 - \sqrt{(2 - 2 \cos 2h)} \\ &= 1 - 2h + \frac{1}{24}(2h)^3 + \dots \end{aligned} \quad \dots (6)$$

$S$  is maximum at the point indicated by  $\eta_0$ , showing that the highest order of extinction or the maximum of the maximum shearing stress does not occur on the periphery.

## (2) Distribution of Stresses on the Contact Area.

The elastic problems of stresses which arise when two cylinders, running parallel with each other, are pressed

together was solved by M. T. Huber and S. Fuchs\* in accordance with Hertz's general theory of contact. In the case where a cylinder ( $E_1, \mu_1$ ) is pressed on a plate ( $E_2, \mu_2$ ), where the bodies in the unstressed state are in contact at the origin of  $(x, y)$ , and where the axis of  $x$  is directed along the common tangent, we may show that the stress-distribution on the contact area can be expressed by the equations

$$w^2 = \frac{4ap'}{\pi} \left\{ \frac{1-\mu_1^2}{E_1} + \frac{1-\mu_2^2}{E_2} \right\},$$

$$\sigma_x = \frac{2p'}{\pi} \frac{y}{w^2} \left[ \sqrt{\frac{v+w^2}{v}} \left\{ 2 - \frac{w^2 y^2}{v^2 + w^2 y^2} \right\} - 2 \right],$$

$$\sigma_y = \frac{2p'}{\pi} \frac{y^3}{v^2 + w^2 y^2} \sqrt{\frac{v+w^2}{v}},$$

$$\tau = \frac{2p'}{\pi} \frac{xy^2}{v^2 + w^2 y^2} \sqrt{\frac{v}{v+w^2}},$$

where

$$2v = (x^2 + y^2 - w^2) + \sqrt{[(x^2 + y^2 - w^2)^2 + 4w^2 y^2]},$$

$2w$  = the width of the contact area,

$a$  = the radius of the cylinder,

$p'$  = the applied force per unit length of the cylinder,

$E, \mu$  = Young's modulus and Poisson's ratio.

On the axis of  $y$  we have, putting  $x=0$ ,

$$\sigma_x = \frac{2p'}{\pi w^2} \left[ \sqrt{y^2 + w^2} \left( 2 - \frac{w^2}{y^2 + w^2} \right) - 2y \right],$$

$$\sigma_y = \frac{2p'}{\pi} (y^2 + w^2)^{-1/2}, \quad \tau = 0.$$

At the origin we get the greatest stress :

$$\sigma_x = \sigma_y = \frac{2p'}{\pi w}.$$

The principal stress difference on the axis of  $y$  may be expressed by the equation

$$S = [\sigma_y - \sigma_{yx}]_{x=0},$$

$$\text{or} \quad S = \frac{4p' y}{\pi w^2} \left[ 1 - \frac{y}{\sqrt{(y^2 + w^2)}} \right].$$

\* *Phys. ZS.* xv. p. 298 (1914).

Differentiating  $S$  with respect to  $y$ , and equating the result to zero, we have  $y_0 = 0.7861 w$ , where  $y_0$  is the value of  $y$ , giving the maximum of  $S$ .

As an example, let a phenolite cylinder ( $a = 17.5$  mm.,  $E_1 = 4.3 \times 10^4$  kg./cm.<sup>2</sup>\*,  $\mu_1 = 0.36$ ) be pressed on a steel plate ( $E_2 = 2 \times 10^6$  kg./cm.<sup>2</sup>,  $\mu_2 = 0.3$ ) so that the pressure  $p'$  ( $P/b$ ) between them is 72.8 kg. (or  $P = 43.7$  kg.,  $b = 0.6$  cm.). Then calculation gives us

$$2w/a = 0.068, \quad y_0/a = 0.027, \quad \eta_0 = 1 - y_0/a = 0.973,$$

the mean intensity of load on the contact area  $= 610$  kg./cm.<sup>2</sup>, the value of stress at the origin  $= 780$  kg./cm.<sup>2</sup>.

In our notation  $2w/a = 2h$ . If we insert  $2h = 0.068$  into the equation (6), we find

$$\eta_0 = 0.965$$

as the position of maximum  $S$  for the case where the uniform pressure  $p$  is distributed radially over the contact area.

### (3) Experiment.

Figs. 5 and 6 (Pl. XV.) show the apparatus employed by the author for measuring the stress-optical effect. For the light source Dr. Nagaoka's mercury lamp is used. The Glan-Thompson's prisms,  $2 \times 2 \times 5$  cm., are employed in the polarizer and analyzer instead of Nicol's prisms. The ray of light from the source reaches the specimen after passing through a condenser, a photographic lens, the polarizer, and another lens in succession. The specimen is then projected by a lens on a photographic plate. The analyzer and a Wratten light filter No. 77 A are placed in front of the camera, which is fitted with a Compur shutter. The lenses used are  $F/4.5$  and  $f = 30$  cm. The quarter-wave plates are removable from the polarizer and the analyzer.

A circular disk of phenolite, 35 mm. in diameter and 6 mm. in thickness, was tested, the initial stresses in it being removed before the test. The disk, placed in the beam of circularly polarized monochromatic light and compressed, as shown in fig. 6 (Pl. XV.), was photographed at the instant so that just one minute had elapsed after being loaded (see fig. 7, Pl. XV.), the applied load being 43.7 kg. (refer to the numerical example in the last article). Since the

\* This value was determined recently and corresponds to  $K_1$ .

value of the coefficient  $K_1$  for phenolite may be taken as  $10.6 \text{ kg./cm.}^*$ , we have in this case

$$4P/\pi a K_1 = 3.$$

Hence fig. 7 (Pl. XV.) should be compared with the theoretical result shown in fig. 4. Fig. 8 (Pl. XV.) was taken at the instant just 15 minutes after being loaded, the load remaining constant. Comparing fig. 7 with fig. 8 (Pl. XV.) proves that isochromatic lines undergo an enormous amount of time effect.

On removing the quarter-wave plates from the apparatus the isoclinic lines were photographed, fig. 9 (Pl. XV.) and fig. 10 (Pl. XVI.), being the typical examples. These should be compared with the theoretical lines as shown in fig. 3.

Measurement on the photographic plate of fig. 7 (Pl. XV.) indicates that the nucleus of the isochromatic lines is inside the periphery, its position being  $\eta_0 = 0.964$ .

For photographing the isochromatic and isoclinic lines the Ilford Screened Chromatic Plates were used, the time of exposure being a tenth of a second. The plates were developed for two and a half minutes at  $20^\circ \text{C.}$  with the hydroquinone developer recommended by Ilford Ltd. for their process plates.

### III. *A Rectangular Thick Plate compressed on its Two Opposite Sides.*

#### (1) *Theory.*

In the case where a rectangular thick plate is compressed by forces applied on its two opposite sides, the stress-components may be expressed in terms of the stress-function  $F$  by the formula

$$\sigma_x = \frac{\partial^2 F}{\partial y^2}, \quad \sigma_y = \frac{\partial^2 F}{\partial x^2}, \quad \tau = -\frac{\partial^2 F}{\partial x \partial y}, \quad \cdot \quad (7)$$

where  $F$  must satisfy the equation

$$\frac{\partial^4 F}{\partial x^4} + \frac{\partial^4 F}{\partial y^4} + 2 \frac{\partial^4 F}{\partial x^2 \partial y^2} = 0.$$

In a rectangular plate, as shown in fig. 11, there are the eight boundary conditions

$$\begin{aligned} [\sigma_x]_{x=0 \text{ or } a} &= 0, & [\sigma_y]_{y=0 \text{ or } b} &= -P(x), \\ [\tau]_{x=0 \text{ or } a} &= 0, & [\tau]_{y=0 \text{ or } b} &= 0. \end{aligned}$$

\* Phil. Mag. xii. p. 503 (1931).

The load  $P(x)$  may be generally developed in a sine series for each value of  $x$  between  $x=0$  and  $x=a$ , namely,

$$P(x) = \frac{4p}{\pi} \sum_{n=1}^{\infty} S_n \sin \frac{n\pi x}{a},$$

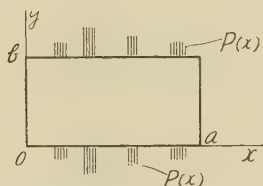
where  $p$  = the intensity of load at any chosen point,

$$S_n = \frac{\pi}{2pa} \int_0^a P(x) \sin \frac{n\pi x}{a} dx.$$

We may introduce a stress-function  $F$  by means of the form

$$F = F_1 + F_2 + F_3,$$

Fig. 11.



where

$$F_1 = \frac{4p}{\pi} \sum_{n=1}^{\infty} A_n \frac{a^2}{n^2 \pi^2} \text{Sech } n\pi \phi_1 \text{Cosh } \frac{n\pi}{a} (y - b/2),$$

$$F_2 = \frac{4p}{\pi} \sum_{n=1}^{\infty} B_n (n\pi \phi_1 + \text{Sinh } n\pi \phi_1)^{-1} \frac{a^2}{n^2 \pi^2} \left\{ \frac{n\pi y}{a} \text{Sinh } \frac{n\pi}{a} (y - b) + \frac{n\pi}{a} (y - b) \text{Sinh } \frac{n\pi y}{a} \right\} \sin \frac{n\pi x}{a},$$

$$F_3 = \frac{4p}{\pi} \sum_{n=1}^{\infty} C_n (n\pi \phi + \text{Sinh } n\pi \phi)^{-1} \frac{b^2}{n^2 \pi^2} \left\{ \frac{n\pi x}{b} \text{Sinh } \frac{n\pi}{b} (x - a) + \frac{n\pi}{b} (x - a) \text{Sinh } \frac{n\pi x}{b} \right\} \sin \frac{n\pi y}{b},$$

$$\phi = a/b, \quad \phi_1 = b/a.$$

Then we have by some calculations

$$\left[ \frac{\partial^2 F}{\partial y^2} \right]_{x=0} = \left[ \frac{\partial^2 F}{\partial y^2} \right]_{x=a} = 0,$$

$$\left[ \frac{\partial^2 F}{\partial x^2} \right]_{y=0} = \left[ \frac{\partial^2 F}{\partial x^2} \right]_{y=b} = - \frac{4p}{\pi} \sum_{n=1}^{\infty} A_n \sin \frac{n\pi x}{a},$$



$$\begin{aligned}
-\left[\frac{\partial^2 F}{\partial x \partial y}\right]_{x=0} &= \left[\frac{\partial^2 F}{\partial x \partial y}\right]_{x=a} \\
&= \frac{4\rho}{\pi} \sum_{n=1}^{\infty} \left[ \sum_{r=1}^{\infty} A_r(Y_{nr}) \right. \\
&\quad \left. + \sum_{r=1}^{\infty} B_r({}_nZ_{r\phi_1}) + C_n \right] \cos \frac{n\pi y}{b}, \\
-\left[\frac{\partial^2 F}{\partial x \partial y}\right]_{y=0} &= \left[\frac{\partial^2 F}{\partial x \partial y}\right]_{y=b} \\
&= \frac{4\rho}{\pi} \sum_{n=1}^{\infty} \left[ A_n \operatorname{Tanh} \frac{n\pi}{2\phi} \right. \\
&\quad \left. + B_n + \sum_{r=1}^{\infty} C_r({}_nZ_{r\phi}) \right] \cos \frac{n\pi y}{a},
\end{aligned}$$

where

$$(Y_{nr}) = \frac{4}{\pi} \frac{1 - \cos n\pi}{2} \frac{r\phi_1}{n^2 + r^2\phi_1^2},$$

$$({}_nZ_{r\phi}) = \frac{8}{\pi} \frac{1 - \cos n\pi}{2} \frac{n^2 r\phi}{(n^2 + r^2\phi^2)^2} \frac{1 + \operatorname{Cosh} r\phi\pi}{r\phi\pi + \operatorname{Sinh} r\phi\pi}.$$

The boundary conditions are satisfied if we put

$$A_n = S_n,$$

$$C_n + \sum_{r=1}^{\infty} B_r({}_nZ_{r\phi_1}) = - \sum_{r=1}^{\infty} A_r(Y_{nr}), \quad . \quad . \quad (8)$$

$$B_n = - \sum_{r=1}^{\infty} C_r({}_nZ_{r\phi}) - A_n \operatorname{Tanh} \frac{n\pi}{2\phi}. \quad . \quad . \quad (9)$$

To make the calculation simpler we eliminate  $B$  from (8) and (9). Then we have the formula for  $C$

$$C_n - \sum_{s=1}^{\infty} \sum_{r=1}^{\infty} ({}_nZ_{r\phi_1})({}_rZ_{s\phi}) C_s = \sum_{r=1}^{\infty} A_r \left[ ({}_nZ_{r\phi_1}) \operatorname{Tanh} \frac{n\pi}{2\phi} - (Y_{nr}) \right].$$

These equations give us three systems of constants,  $A$ ,  $B$ , and  $C$ . Now all the constants being known, the expressions for the stress-components can be found from (7).

## (2) Numerical example.

A square plate, as shown in fig. 12, is considered.

The intensity of load for  $0 \leq x < 0.4a$  is zero,

„ „  $0.4a \leq x \leq 0.6a$  is  $p$ ,

„ „  $0.6a < x \leq a$  is zero.

The load may be expressed by the equation

$$P(x) = \frac{4p}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \sin \frac{n\pi}{2} \sin \frac{n\pi}{10} \sin \frac{n\pi x}{a}.$$

Calculation gives us the coefficients and stresses as shown in Table I. and figs. 13 and 14.

Fig. 12.

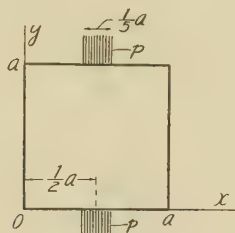


TABLE I.

$n$ .	$A_n$ .	$-B_n$ .	$-C_n$ .
1.....	0.3091	0.2652	0.0396
3.....	-0.2697	-0.2803	0.0112
5.....	0.2	0.1923	0.0139
7.....	-0.1156	-0.1211	0.0099
9.....	0.0343	0.0292	0.0071
11.....	0.0281	0.0238	0.0056
13.....	-0.0622	-0.0660	0.0045
15.....	0.0667	0.0634	0.0038
17.....	-0.0476	-0.0504	0.0032
19.....	0.0163	0.0137	0.0028
21.....	0.0147	0.0123	0.0025
23.....	-0.0352	-0.0373	0.0023
25.....	0.04	0.0381	0.0020

As a measure of the accuracy of these calculations the value of  $\int_0^a \sigma_y dx$  is measured graphically at the sections parallel to the axis of  $x$ , which must be compared with  $P=0.2 ap$ .

TABLE II.

## Measure of Accuracy.

Sections.	Measured values.	Errors in percentage.
$y = 0.2 a$	0.2008 $ap$	+0.4
$y = 0.3 a$	0.2002 $ap$	+0.1
$y = 0.4 a$	0.1984 $ap$	-0.8
$y = 0.5 a$	0.1992 $ap$	-0.4

Thus the error is comparatively small.

Fig. 13.

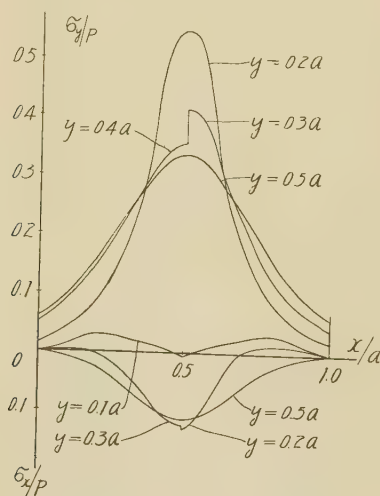
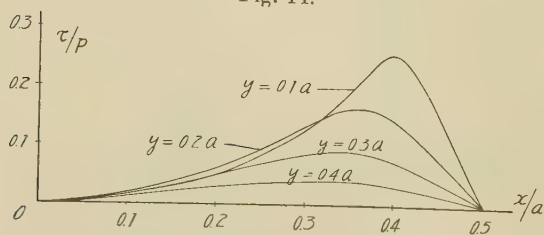


Fig. 14.



The principal stress difference  $S$  at a point may be expressed by the form  $S = mp$ , where  $p$  is the intensity of load as before and  $m$  is the numerical coefficient calculated from the stress-components. If we insert the two relations

$$p = P/0.2 ad, \quad Sd = nK,$$

into the above expression,  $S=mp$ , we get

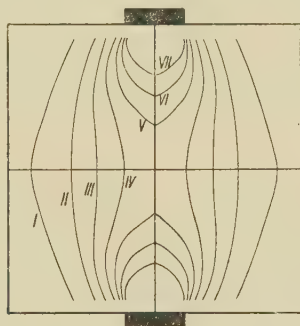
$$n = 5mP/aK.$$

Further, assuming

$$P/aK = 2, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and calculating the values of  $m$  at various points, the values of  $n$  at various points are then found. The loci of the integral values of  $n$  (the theoretical isochromatic lines) are finally traced as shown in fig. 15, where the Roman numerals show the order of extinction or the values of  $n$ .

Fig. 15.



### (3) Experiment.

A square plate of phenolite,  $33 \times 33 \times 6$  mm., was tested. The isochromatic lines were photographed at the instant just one minute after being loaded, the load being 70 kg. (fig. 16, Pl XVI.). Since the coefficient  $K_1$  for phenolite may be taken as 10.6 kg./cm., we have in the present specimen

$$P/aK_1 = 2,$$

which is nothing but the equation (10). Hence fig. 16 (Pl. XVI.) should be compared with the theoretical lines shown in fig. 15.

Figs. 17, 18, 19, and 20 (Pl. XVI.) show the typical examples of isoclinic lines. In fig. 17 we may find that the directions of principal axes at the section  $x=0.5a$  or  $y=0.5a$  are vertical and horizontal, which agrees clearly with the theory.

IV. *Conclusion.*

1. In the scope of this paper it may be concluded that the values of stresses experimentally obtained by *the law of photo-elastic extinction* are in fairly good agreement with the theoretical values.

2. Further investigations are needed to determine whether the accuracy and usefulness of this law may be established for general purposes of studying two-dimensional elastic systems.

N.B.—Dr. Z. Tuzi, Research Member of the Institute of Physical and Chemical Research in Tokyo, recently informed the author that the elastic properties of phenolite seem to differ to some extent according to the baking temperature in its finishing stage, and that the higher the temperature (limits being  $100^{\circ}\sim 140^{\circ}$  C.) the harder and brittler becomes phenolite. If it is really so, the value of the coefficient  $K$  may also differ. Hence the value of  $K$  should be determined whenever a new plate of phenolite is used.

LXXVI. *Arc, Spark, and Glow: a Note on Nomenclature.*  
By JOHN THOMSON, M.A., B.Sc., Ph.D., Lecturer in  
*Natural Philosophy at the University of Glasgow* \*.

THE purpose of this note is two-fold. First, it is proposed to call attention to ambiguities of terminology which exist with regard to the electric discharge. Three classes of investigators—the electrical engineers, those engaged in research upon the mechanism of the gaseous discharge, and the spectroscopists—employ the terms “arc” and “spark” to define certain discharge phenomena. Unfortunately, the connotation of each term varies considerably from one class to the other, so that auxiliary definition is always required, but too seldom given. By physicists in general the terms are used in the sense which was originally intended by the electrical engineers, but, as the progress of research has shown that the phenomena described by them are complex, the words have become not only ambiguous but definitely misleading. The attempt will therefore be made to indicate clearly what each of the three classes mentioned intends to be understood when the term “arc” or “spark” is employed.

\* Communicated by the Author.



Secondly, it is proposed to describe a simple experiment which exhibits at atmospheric pressure all the types of electric discharge. From a consideration of the conditions under which each type appears it should be possible to suggest some more exact definitions which will rationalize the nomenclature and destroy the confusion which at present exists.

*Electrical Engineering Nomenclature.*

In the 'Dictionary of Applied Physics' an electric "spark" is defined as "the sudden discharge of electricity across an air-gap accompanied by the production of light and heat," and the "arc" as "a stream of hot gases carrying an electric current across a gap between two electrodes." Surely these two definitions are not mutually exclusive; it is easy to imagine a spark (so defined) taking the form of an arc (so defined). Yet in practice a distinction between the two is implied. This may be well exemplified with reference to the phenomena exhibited by an induction coil or high-tension magneto.

*I. Induction Coil Discharges without a Secondary Condenser.*—Suppose the secondary terminals of a coil to be connected to an air-gap with no condenser in parallel, and the primary current to be arranged so that a bright discharge across the gap takes place. Then the evidence of the rotating mirror<sup>(1)</sup> is that at each break in the primary circuit there is a series of secondary discharges. The first of these is bright, particularly at the outset, and the others are faint. The current is pulsating but unidirectional. A simultaneous oscillograph record of the potential across the secondary coil is of the form shown in fig. 1<sup>(2)</sup>, where the ordinate measures the square of the secondary potential and the abscissa the time.

The potential peak A gives rise to the first bright discharge, while B, C, D, E are the cause of the fainter, more diffuse ones. In accordance with the customary terminology of electrical engineering, discharge A is called a "spark" and B, C, D, E are called "arcs." The number of arcs which follow the spark depends, of course, upon experimental conditions; it is even possible, by using larger primary currents and small gaps, to obtain a decaying aperiodic arc instead of the pulsations of fig. 1.

It is difficult to say exactly what is the distinguishing characteristic of the spark in this discharge. Certainly A is considerably brighter than B, C, D, E. In fact, the aggregate intensity of the last four is usually small compared with

the intensity of the spark. There is also evidence that the initial part of discharge A is of a different nature from the rest—it is the earlier stage which is most brilliant. But neither of these qualities is of much use in forming a definition. Perhaps the best properties of the spark which can be used to distinguish it from the arc are the potential difference required for its production and the time which it takes to occur. A is associated with a very large potential difference between the electrodes—something of the order of 20,000 volts/cm. in air at atmospheric pressure, while in B, C, D, E the corresponding inter-electrode potential difference is less than one-tenth of this. Also, the initial spark is of very

Fig. 1.

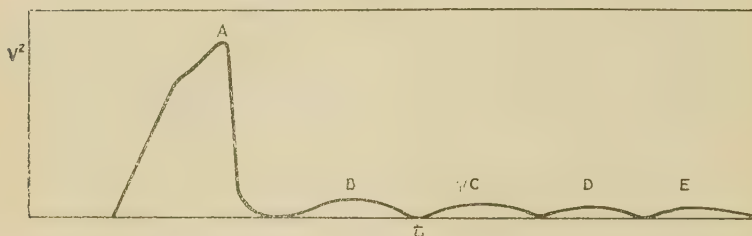
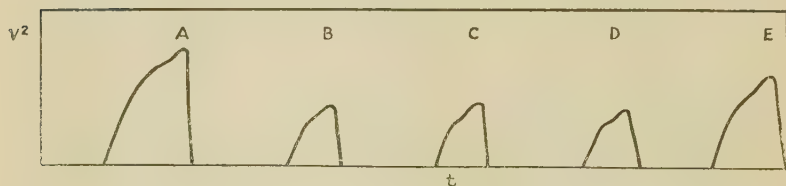


Fig. 2.



short duration. It is a sudden rush of electricity accompanied, as is seen from fig. 1, by a very rapid decrease of potential.

II. *Induction Coil Discharge with a Secondary Condenser.*—Suppose, now, a condenser to be placed in parallel with the air-gap, and the primary current again arranged so that bright discharges are obtained. In this case one break of the primary circuit gives rise to a series of discharges of a different type. These, when examined by means of the rotating mirror, prove to be all fairly bright, the first and last being slightly brighter than the others. An oscillograph record of the secondary potential is of the general appearance of fig. 2.

In this case each discharge A, B, C, D, E is called a spark, and each presents the general appearance of A of the discharge without a condenser. Often each discharge of this type contains more than one spark—there may be as many as six associated with one potential peak. If the primary current is greatly increased, a time comes when the *regime* of fig. 1 begins in a modified way. The pulsating arc makes its appearance, and the number of sparks is reduced to one or two, corresponding to one or two distinct potential peaks. Again, it is evident that the most constant property of the spark is the high associated potential. All the peaks A, B, C, D, E are of the order 20,000 volts/cm., although in general they are not so large as A of fig. 1. Hence it seems that the common usage of electrical engineering terminology is simply to associate the name “spark” with a bright high-potential discharge.

*Nomenclature employed in connexion with the Gaseous Discharge.*

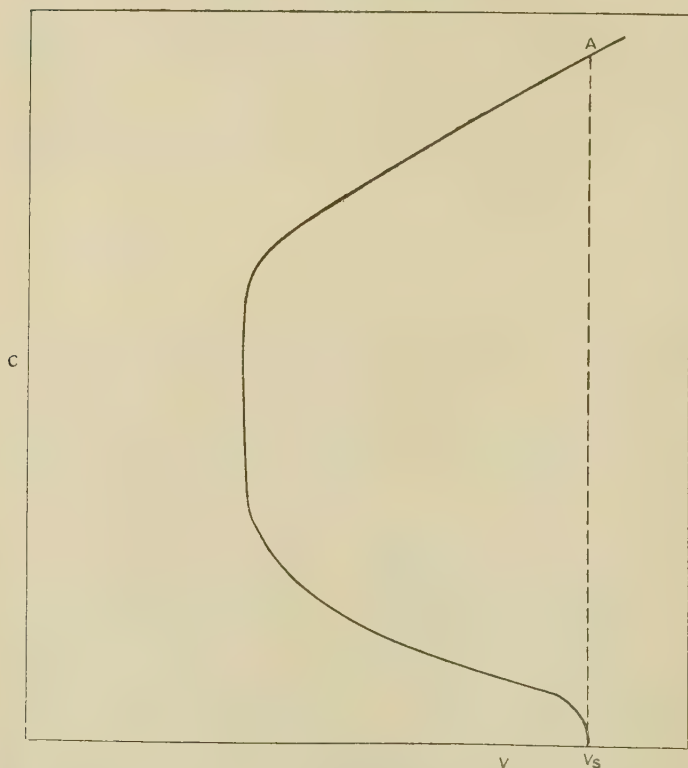
The mechanism of what has been called by modern physicists the “spark discharge” has been the subject of innumerable investigations. In this connexion the word “spark” is seldom used as a substantive, the “sparking potential” being the important concept. If, however, the spark is to be defined at all, then it must be as *the initial stage of any discharge of electricity through a gas, where the current is carried entirely by gaseous ions between cold electrodes*. The “sparking potential” is the minimum steady potential which, when applied for an indefinite time between the electrodes, produces an appreciable current through the gas; it is a function of the nature and pressure of the gas, the shape of the electrodes and their distances apart, and, probably, the photoelectric emissivity of the electrode surfaces.

These definitions imply a considerable knowledge of the nature of the discharge, and the wording of the definition of the spark is particularly significant. It is now well known that the general shape of the current-potential characteristic of a gas discharge between cold electrodes is as shown in fig. 3, where the abscissa measures the potential difference between the electrodes, and the ordinate the current flowing in the discharge. Such characteristics have been carefully studied by Taylor, Penning, and Clarkson<sup>(3)</sup>.

It follows from the nature of this curve that although the potential difference between the electrodes must be raised to

$V_s$  (fig. 3) to start the discharge, the latter may be maintained at a much smaller voltage. Hence, if the current in any experiment is not controlled by resistance in the circuit, immediately after the discharge commences the conditions correspond to point A on the characteristic. This is the reason for defining the spark as the *initial stage* of the discharge. The curve shown in fig. 3 is really a corona and

Fig. 3.



glow characteristic; the spark is represented by an infinitesimally small portion of the curve at  $V_s$ .

It is rather more difficult to suggest a definition of the arc which will be representative of the nomenclature employed in connexion with the gaseous discharge. As distinct from the spark, the arc in this connexion is to be associated with a hot cathode at which thermionic emission is taking place. In practice, however, unless a heated filament of tungsten or some other metal of high boiling-point

is intentionally used as the cathode, thermionic emission requires that the latter should be at such a temperature that it will be partly vaporized. Hence, leaving out of account special techniques, an arc is a discharge in which the current is carried by the metal vapour as well as the gas. This definition forms a sufficiently marked contrast to that of the spark.

Comparing these definitions with the loose ideas acquired from a study of the engineer's use of the terms arc and spark, it is immediately obvious that some readjustment of nomenclature is necessary. The rather ghostly spark of the researcher on the mechanism of the discharge is so faint as to be almost invisible, and the maximum current passing during such a *régime* is of the order of microamperes. The typical engineer's spark results from the discharge of a large condenser. It is of enormous light-intensity, and the current in it is of the order of hundreds of amperes.

#### *The Nomenclature of Spectroscopy.*

Only a word is required in this connexion. The "arc" spectrum of an element is that produced when the atom or molecule is returning to its normal state from one of higher energy. It is therefore typical of the un-ionized element, or in the extreme case of the recombination of an electron with a singly ionized atom or molecule. The "spark" spectrum or enhanced spectrum is that produced by the ionized element returning to its most stable ionized state. In the extreme case it is produced by a multiply-ionized atom or molecule recombining with an electron. The use of the terms "arc" and "spark" in this manner arose from the empirical study of spectra before the analysis given above was understood. It was found that certain lines in the complete spectrum of an element were not present when the substance was excited by an arc discharge, but were present in the spark. The arcs and sparks which are meant are, of course, those defined by the terminology of the engineers. It is now known that the excitation of the enhanced spectrum depends upon high current density and high electric field strength. These are characteristic of the engineer's spark—hence the connexion. Yet the spectra exhibited by a typical spark discharge are indeed varied. Four spectra are obtained with varying degrees of intensity: (a) the arc spectrum of the gas between the electrodes; (b) the spark spectrum of the gas; (c) the arc spectrum of the metal of the electrodes; (d) the spark spectrum of the metal. In no case is the total intensity of the two spark spectra as large as that of the

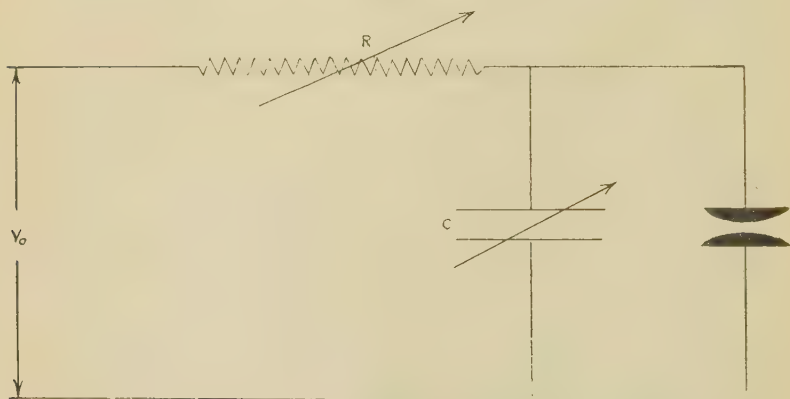


other two. The spark actually enhances the arc spectrum in addition to causing the spark lines to appear. If the spectra of the gas between the electrodes are required no condenser is used. Under such circumstances, so long as the discharge current is small, only a few faint metal lines appear. If, however, a condenser is placed across the gap, the spectra of the metal electrodes become brighter and the gaseous spectra are partially masked. The explanation of these spectral phenomena will appear when the details of such discharges are considered later.

*Spark, Glow, and Arc at Atmospheric Pressure.*

A simple circuit which exhibits all types of discharge at atmospheric pressure is shown in fig. 4. The variable con-

Fig. 4.



denser  $C$ , shunted by a spark-gap is connected to a direct-current high-voltage supply through the variable resistance  $R$ . In the experiment performed by the writer the spark-gap electrodes were copper spheres 3 cm. in diameter, and the supply voltage was about 1600.  $R$  could be varied from 2 to 0.1 megohms, and  $C$  in steps from 2 to less than 0.0001 microfarads. A microscope was focussed on the gap. The type of discharge obtained depends on the values of  $R$  and  $C$ .

**I. Capacity Discharges.**—With  $C$  of the order of a microfarad, and the gap adjusted so that sparks would pass at 1500 volts (gap about 0.05 mm. in length), regular discontinuous discharges were obtained, the time between each depending upon the value of  $R$ . With  $C = 2\mu\text{F}$ , and  $R = 2$  megohms, about 13 seconds elapsed between each discharge.

The time was reduced to 1 second, when  $R$  was equal to 0.2 megohms. In fact, as a simple analysis of the circuit shows, the time  $t$  between two successive discharges is given by the equation  $t = AC R$ , where  $A$  is a constant depending upon the length and nature of the air-gap. Each discharge of this type is bright, and, of course, carries a large current. The latter is oscillatory, being due to the discharge of the condenser, and typical in every way of the engineer's spark. It may be noted that the spectrum of the radiation emitted from such slow flashes is a mixture of copper and air lines, but by far the greater part of the light is due to the band spectrum of nitrogen.

If  $C$  is gradually decreased the flashes become more and more frequent, until, when  $C = 0.001 \mu F$  and  $R = 0.2$  megohms, the circuit emits an audible note of frequency about 200/sec. At the same time the spectrum of the radiation emitted undergoes a change. The copper lines become more prominent relative to the air; when  $C$  is less than  $0.001 \mu F$ , the discharge is distinctly green in colour, indicating the presence of intense copper radiation.

II. *The Glow Discharge.*—If the condenser capacity is still further reduced, a time comes when the intermittent discharges, each of an oscillatory nature, cease abruptly, and an entirely different *régime* begins. The discharge is now continuous and unidirectional; it is, indeed, a typical glow. The negative electrode is partly covered by a blue disk—the cathode glow, the area of which appears to vary directly with the current. Immediately beyond this is the Faraday dark space, while beyond that again is the red positive column, occasionally faintly striated and ending in a bright anodic spot. These details can, of course, only be seen under the microscope; if higher potentials are used in the hope that the glow may be lengthened, convection currents of air in the gap bend the positive column so far upwards that the glow is extinguished.

This glow discharge at atmospheric pressure has been noted and partly investigated on numerous occasions. It has been observed in researches on the arc<sup>(4)</sup>, but it was discovered and has been further analysed during researches on the mechanism of the gaseous discharge<sup>(5)</sup>. The writer cannot find that it is any way different from the typical low-pressure glow either with regard to its appearance and spectrum or with regard to the ionization phenomena involved. The band spectrum of nitrogen is responsible for almost all the light emitted, but, as the current is increased, the green

copper lines begin to be prominent. If the resistance  $R$  is continuously decreased ( $C$  being approximately zero), the glow degenerates into the "true arc," and the copper spectrum completely gains the ascendancy.

Thus by varying  $C$  and  $R$  it is possible, with the simple apparatus described to demonstrate all the phenomena usually entitled "arc," "spark," and "glow." A consideration of the mechanism of each in this simple case is helpful in formulating exact definitions.

*Characteristics of the "Spark."*—The discharge which usually goes by this name is obviously to be associated with the discharge of a condenser. All sparks, in other words, are capacity effects. Sparks may be obtained at any gas pressure, and indeed all the effects mentioned above in connexion with air at atmospheric pressure are obtainable at pressures as low as a tenth of a millimetre of mercury. It is, however, more difficult to obtain regular sparking of a small condenser at low pressures. This is to be attributed to the greater mobility of the ions. Even in the case of the "uncondensed" discharge of an induction coil, the capacity of the secondary is sufficient to produce the first spark. Indeed, if the resistance in the experiment described is made sufficiently high, the capacity of the gap itself is sufficient to prohibit the formation of the unidirectional glow. There can be no hesitancy, therefore, about associating the discharge commonly called a spark with the discharge of a capacity. Yet, even if the analysis given has succeeded in properly classifying this discharge, it has not made the common nomenclature more palatable. The condenser discharge is a *mixed* one; it contains at least two ionizing factors, which can hardly be associated in a fundamental definition. As has been observed, rapidly recurring "sparks" cause a large rise in temperature of the electrodes, so that metal vapour is liberated, thus introducing an "arc" element into the discharge. Although this is not present to the same extent in slow flashes, the tendency exists, and in condensed induction coil discharges the metal vapour plays an important part. The writer is therefore of the opinion that the terms to denote typical discharges should be redefined in terms of the knowledge we now possess of the processes at work.

#### *Suggestions as to Rationalisation.*

It is suggested that the nomenclature of the investigators of the gaseous discharge should be universally adopted. The following definitions would result:—

*Spark.*—The initial unstable stage in any discharge between cold electrodes.

The spark thus defined is associated with the sparking potential which may be measured, but the spark itself is a condition rather than an observable phenomenon.

*Arc.*—A discharge in which the current is carried by the metal of the electrodes as well as the gas between them.

This is an observable state. The definition takes no account of special techniques for the production of gaseous arcs by means of externally stimulated thermionic emission.

*Glow.*—A discharge between cold electrodes, when the current is entirely carried by gaseous ions.

Again this is an observable state so long as the energy given to the gap is controlled by external resistances.

To exemplify the connexions between these discharges, consider the following hypothetical experiment. A direct-current potential difference is applied across an air-gap in parallel with which there is no capacity, and in series with which there is no resistance. What will occur?

As soon as the potential difference is equal to the “static sparking potential” for the given gap, a small capacity discharge will take place. This in its initial stage is a spark, but, owing to the shape of the glow characteristic (fig. 3), it becomes a glow almost immediately. Simultaneously the capacity oscillations die out. The glow is then carrying a current of a few milliamperes. If the electrodes are of such a nature that a high temperature develops at the points where the discharge is occurring (low heat conductivity), and if the boiling-point of the cathode is lower than the temperature reached (which will usually be the case), some of the metal is vaporized. This increases the current, since the ionizing potential of the metal is lower than that of the gas. Hence a higher temperature is developed. The process is cumulative, and in a very short time the discharge takes the form of an arc. Since this amounts to short-circuiting the gap, the current is only limited by the power available.

In general, electric discharges are mixed, containing both of the components, arc and glow. Of this nature is the induction coil discharge, whether condensed or uncondensed. A consideration of the power available in each case explains the types of spectra which are obtained.

The writer wishes to thank Professor Taylor Jones for his helpful criticism. The experimental work described was performed in the Research Laboratories of the Natural Philosophy Department of the University of Glasgow.

## References.

- (1) E. Taylor Jones, 'The Theory of the Induction Coil,' p. 147, fig. 61.
- (2) E. Taylor Jones, *op. cit.* p. 150, fig. 64.
- (3) Taylor and Sayce, *Phil. Mag.* i. p. 918 (1925); Penning, *Phys. Zeits.* xxvii. p. 187 (1926); Taylor, *Phil. Mag.* iii. p. 368, p. 753 (1926).
- (4) H. Simon, *Phys. Zeits.* viii. p. 471 (1907); Grotrian, *Ann. d. Phys.* xlvii. p. 141 (1915); Stark, *Ann. d. Phys.* xii. p. 692 (1903); Burstyn, *Electrotech. Zeits.* p. 503 (1920); Chrisler, *Astrophys. J.* liv. p. 273 (1921); Slepian, *Frank. Inst. J.* cci. p. 79 (1926).
- (5) Toepler, *Wied. Ann.* lxiii. p. 109 (1897), lxvi. p. 671 (1898); Kauffmann, *Ann. d. Phys.* ii. p. 158 (1900); Aubertin, *Le Radium*, ix. p. 186 (1912); Melcion, *Comptes Rendus*, clxxxix. p. 112 (1929).

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LXXVII. *Wave Equations of an Electron in a real form.*  
By D. MEKSYN, *Ph.D.*, *Mathematical Department, Edinburgh University* \*.

§1. *Introduction and Summary.*

AS it is known the wave equations of an electron are imaginary expressions; so are their solutions. It seems as if imaginary quantities are inherent in the wave mechanics.

In the present paper an attempt is made to present the wave equations and their solutions in a real form.

In a recent publication † I have derived Dirac's equations in a five-dimensional invariant form, and these equations, slightly modified for the case of an external electromagnetic field, may be presented in a real five-dimensional form.

It is proved that in the case when Dirac's equations have imaginary periodic solutions of the form  $\psi e^{\frac{2\pi i}{h} Wt}$  our equations have a solution of the form

$$\lambda \cos \frac{2\pi}{h} (mcx_5 - Wt) + \mu \sin \frac{2\pi}{h} (mcx_5 - Wt), \quad (1)$$

where  $\lambda$  and  $\mu$  are real functions.

Evaluating the energy tensor we obtain the characteristic difference of energies at transitions—namely, we get the following expression:

$$A \cos \frac{2\pi}{h} (W_1 - W_2)t + B \sin \frac{2\pi}{h} (W_1 - W_2)t, \quad (2)$$

\* Communicated by the Author.

† *Phil. Mag.* [7] ix. p. 568 (1930).



where A and B are functions of the space variables; the five-dimensional term  $mcx_5$  drops out from the energy tensor.

The real equations solve the difficulty mentioned by Dirac \*, namely, that the same relativity wave equations are valid for particles of opposite charges; this is due to the imaginary terms in these equations.

As our equations are real, this difficulty does not arise in our case; the equations and their solutions are different for positive and negative particles.

It seems that the five-dimensional space represents a natural system of reference for the wave equations.

## §2. Equations for Free Motion.

The equations are derived from the Hamiltonian Principle (Phil. Mag. *ibid.*). The field is described by an anti-symmetric tensor of the second rank in five dimensions. The tensor has ten components, four of which are complex, and two scalar functions are introduced as a result of the variational problem, in all sixteen equations.

The equations, thus obtained, are analogous to Maxwell's, the latter being merely a four-dimensional projection of the former. They are

$$\frac{\partial F_{\alpha\beta}}{\partial x_\beta} + \frac{\partial \mu}{\partial x_\alpha} = 0, \quad \alpha, \beta = 1, 2, 3, 4, 5 \quad (3)$$

and

$$\left. \begin{aligned} \frac{\partial F_{\alpha\beta}}{\partial x_\gamma} + \frac{\partial F_{\beta\gamma}}{\partial x_\alpha} + \frac{\partial F_{\gamma\alpha}}{\partial x_\beta} + \frac{\partial G_{55}}{\partial x_5} + \frac{\partial \lambda}{\partial x_\delta} &= 0, \\ \frac{\partial G_{5i}}{\partial x_i} + \frac{\partial \lambda}{\partial x_5} &= 0, \end{aligned} \right\} \quad (4)$$

$$\alpha, \beta, \gamma, \delta = 1-4, \quad i = 1-5.$$

The expressions (3) and (4) comprise ten equations, and the six remaining are

$$\frac{\partial F_{\alpha\beta}}{\partial x_5} = \frac{\partial F_{\alpha 5}}{\partial x_\beta} - \frac{\partial F_{\beta 5}}{\partial x_\alpha} + \frac{\partial G_{\delta 5}}{\partial x_\gamma} - \frac{\partial G_{\gamma 5}}{\partial x_\delta}, \quad (5)$$

$$\alpha, \beta, \gamma, \delta = 1-4.$$

In order to make these equations real we assume that the following components are purely imaginary:—

$$F_{12}, \quad F_{31}, \quad F_{12}, \quad \mu, \quad F_{15}, \quad F_{25}, \quad F_{35}, \quad G_{45}, \quad x_4 = ict.$$

If we substitute  $iF_{12}, \dots$  in (3), (4), (5) instead of  $F_{12}, \dots$  we obtain sixteen real equations. They can, however, be combined into eight real equations. It appears that for our purpose eight functions suffice.

We denote

$$\left. \begin{aligned} F_{14} + F_{15} &= \phi_1, & F_{24} + F_{25} &= \phi_2, \\ & F_{34} + F_{35} &= \phi_3, & \lambda + G_{45} &= -\phi_4, \\ F_{23} - G_{15} &= \phi_5, & F_{31} - G_{25} &= \phi_6, \\ & F_{12} - G_{35} &= \phi_7, & \mu + F_{45} &= \phi_8, \end{aligned} \right\} \quad (6)$$

and combining in two's the equations (3), (4), and (5) we easily obtain

$$\left. \begin{aligned} \left( -\frac{\partial}{c\partial t} + \frac{\partial}{\partial x_5} \right) \phi_1 + \frac{\partial \phi_7}{\partial x_2} - \frac{\partial \phi_6}{\partial x_3} + \frac{\partial \phi_8}{\partial x_1} &= 0, \\ \left( -\frac{\partial}{c\partial t} + \frac{\partial}{\partial x_5} \right) \phi_2 - \frac{\partial \phi_7}{\partial x_1} + \frac{\partial \phi_5}{\partial x_3} + \frac{\partial \phi_8}{\partial x_2} &= 0, \\ \left( -\frac{\partial}{c\partial t} + \frac{\partial}{\partial x_5} \right) \phi_3 + \frac{\partial \phi_6}{\partial x_1} - \frac{\partial \phi_5}{\partial x_2} + \frac{\partial \phi_8}{\partial x_3} &= 0, \\ \left( -\frac{\partial}{c\partial t} + \frac{\partial}{\partial x_5} \right) \phi_4 - \frac{\partial \phi_5}{\partial x_1} - \frac{\partial \phi_6}{\partial x_2} - \frac{\partial \phi_7}{\partial x_3} &= 0, \\ \left( \frac{\partial}{c\partial t} + \frac{\partial}{\partial x_5} \right) \phi_5 + \frac{\partial \phi_3}{\partial x_2} - \frac{\partial \phi_2}{\partial x_3} + \frac{\partial \phi_4}{\partial x_1} &= 0, \\ \left( \frac{\partial}{c\partial t} + \frac{\partial}{\partial x_5} \right) \phi_6 - \frac{\partial \phi_3}{\partial x_1} + \frac{\partial \phi_1}{\partial x_3} + \frac{\partial \phi_4}{\partial x_2} &= 0, \\ \left( \frac{\partial}{c\partial t} + \frac{\partial}{\partial x_5} \right) \phi_7 + \frac{\partial \phi_2}{\partial x_1} - \frac{\partial \phi_1}{\partial x_2} + \frac{\partial \phi_4}{\partial x_3} &= 0, \\ \left( \frac{\partial}{c\partial t} + \frac{\partial}{\partial x_5} \right) \phi_8 - \frac{\partial \phi_1}{\partial x_1} - \frac{\partial \phi_2}{\partial x_2} - \frac{\partial \phi_3}{\partial x_3} &= 0, \end{aligned} \right\} \quad (7)$$

These equations can be reduced to Darwin's\*.

### §3. *Equations for the Case of an External Electromagnetic Field.*

We now consider the case of an external electromagnetic field. For a free electron the equation of momenta is

$$\frac{E^2}{c^2} - p_1^2 - p_2^2 - p_3^2 = m^2 c^2. \quad \dots \quad (8)$$

We assume that  $mc = p_5$  is the momentum associated with the fifth dimension.

\* Proc. Roy. Soc. A, cxviii. p. 658.

The wave function becomes accordingly

$$\psi \sim e^{\frac{2\pi i}{h}(p_1x_1 + p_2x_2 + p_3x_3 + p_5x_5 - Et)}, \quad . \quad . \quad . \quad (9)$$

where  $E$  is positive.

Suppose now that we have an external electromagnetic field. In that case we know that instead of  $\frac{\partial}{c\partial t}$  and  $\frac{\partial}{\partial x_r}$  we have to substitute in our equations the expressions

$$\frac{\partial}{c\partial t} - \frac{2\pi i e V}{h c} \quad \text{and} \quad \frac{\partial}{\partial x_r} + \frac{2\pi i e}{h c} A_r.$$

We substitute, however, instead of  $\frac{\partial}{c\partial t}$  and  $\frac{\partial}{\partial x_r}$ , the following forms (for the case of an electron):

$$\frac{\partial}{c\partial t} - \frac{eV}{mc^2} \frac{\partial}{\partial x_5}, \quad \frac{\partial}{\partial x_r} + \frac{eA_r}{mc^2} \frac{\partial}{\partial x_5}, \quad r=1, 2, 3. \quad (10)$$

The equations (7) remain real; the wave functions enter all terms through their differential coefficients of the first order. We can combine the eight equations (7) into Dirac's four equations. We shall have then to solve them by imaginary quantities.

#### §4. The Law of Conservation.

Multiplying (7) by  $\phi_1, \phi_2, \dots$  and combining the eight equations we easily find

$$\left. \begin{aligned} \rho &= -\frac{1}{c} \left[ \frac{\phi_1^2 + \phi_2^2 + \dots + \phi_4^2 + \phi_5^2 + \dots + \phi_8^2}{2} \right], \\ j_1 &= [\phi_1\phi_8 - \phi_2\phi_7 + \phi_3\phi_6 - \phi_4\phi_5], \\ j_2 &= [\phi_1\phi_7 - \phi_3\phi_5 + \phi_2\phi_8 - \phi_4\phi_6], \\ j_3 &= [\phi_2\phi_5 - \phi_1\phi_6 + \phi_3\phi_8 - \phi_4\phi_7], \\ j_5 &= \frac{eV}{mc^2} \rho + \frac{e}{mc^2} [A_1j_1 + A_2j_2 + A_3j_3] + H, \end{aligned} \right\} \quad . \quad (11)$$

where

$$H = \left[ \frac{\phi_1^2 + \dots + \phi_4^2 - \phi_5^2 - \dots - \phi_8^2}{2} \right]. \quad . \quad . \quad (12)$$

The law of "conservation" becomes

$$\frac{\partial j_1}{\partial x_1} + \frac{\partial j_2}{\partial x_2} + \frac{\partial j_3}{\partial x_3} + \frac{\partial \rho}{\partial t} + \frac{\partial j_5}{\partial x_5} = 0. \quad . \quad . \quad (13)$$

In order that conservation shall take place it is necessary that the last term in (13) shall vanish, or

$$\frac{\partial j_5}{\partial x_5} = 0,$$

or, what comes to the same thing, that the current densities  $\rho, j_1, j_2, j_3$  shall be independent of  $x_5$ .

The fifth component in (11) is rather complicated. For the case of a free electron, if  $\rho$  is equal to the energy  $E$ , the current is equal to  $p_1, p_2, p_3$  and  $j_5 = mc$ , where  $p_1 \dots$  are the momenta of a moving electron, and  $m$  is the invariant mass; thus in this case the fifth component has a simple physical interpretation.

### §5. Comparison with Dirac's Equations.

We find now the connexion between the functions  $\phi$  and Dirac's  $\psi$ .

Dirac's equations are

$$\left. \begin{aligned} (p_0 + mc)\psi_1 + (p_1 - ip_2)\psi_4 + p_3\psi_3 &= 0, \\ (p_0 + mc)\psi_2 + (p_1 + ip_2)\psi_3 - p_3\psi_4 &= 0, \\ (p_0 - mc)\psi_3 + (p_1 - ip_2)\psi_2 + p_3\psi_1 &= 0, \\ (p_0 - mc)\psi_4 + (p_2 + ip_2)\psi - p_3\psi_2 &= 0, \end{aligned} \right\} \quad (14)$$

where

$$p_0 = -\frac{h}{2\pi i c} \frac{\partial}{\partial t} + \frac{e}{c} V; \quad p_1 = \frac{h}{2\pi i} \frac{\partial}{\partial x_1} + \frac{e}{c} A_1. \quad (15)$$

Multiplying the first equation (7) by  $i$ , and subtracting from the second, we find that the obtained expression is equivalent to the second equation in (14) (in our expressions  $\frac{\partial}{\partial x_5}$  appears instead of  $mc$ ). Performing similar transformations with the remaining equations (7), and comparing the obtained results with (14), we arrive at the following connexion between the functions  $\phi$  and  $\psi$  :—

$$\left. \begin{aligned} \psi_1 &= \phi_4 - i\phi_3, & \psi_2 &= \phi_2 - i\phi_1, \\ \psi_3 &= -\phi_7 - i\phi_8, & \psi_4 &= -\phi_5 - i\phi_6 \end{aligned} \right\} \quad (16)$$

### §6. Solution of the Equations.

We shall now prove that in all cases, when Dirac's equations have imaginary periodic solutions, the real equations have real periodic solutions.

We consider the general case of an external electromagnetic field, and assume that the periodic solutions depend upon time in the following way :—

$$\phi \sim \frac{\sin \alpha}{\cos \alpha}, \quad \alpha = \frac{2\pi}{h} (mcx_5 - Wt). \quad . \quad . \quad (17)$$

A glance at the equations (7) and (10) shows that in the general case they cannot be satisfied by a simple sine or cosine solution, but must be a combination of both.

We assume accordingly for the  $\phi$ 's the following expressions :—

$$\left. \begin{aligned} \phi_1 &= -\lambda_2 \sin \alpha - \mu_2 \cos \alpha, & \phi_5 &= -\lambda_4 \cos \alpha + \mu_4 \sin \alpha, \\ \phi_2 &= \lambda_2 \cos \alpha - \mu_2 \sin \alpha, & \phi_6 &= -\lambda_4 \sin \alpha - \mu_4 \cos \alpha, \\ \phi_3 &= -\lambda_1 \sin \alpha - \mu_1 \cos \alpha, & \phi_7 &= -\lambda_3 \cos \alpha + \mu_3 \sin \alpha, \\ \phi_4 &= \lambda_1 \cos \alpha - \mu_1 \sin \alpha, & \phi_8 &= -\lambda_3 \sin \alpha - \mu_3 \cos \alpha, \end{aligned} \right\} \quad . \quad . \quad . \quad (18)$$

Inserting these values of  $\phi$  in (7), and equating to zero separately the cofactors of  $\sin \alpha$  and  $\cos \alpha$ , we obtain sixteen equations for the eight functions  $\lambda$  and  $\mu$ ; there are, however, only eight different equations, and they can be combined into four, which are found to be Dirac's equations.

Thus we obtain the following connexion between Dirac's functions  $\psi$  and the  $\lambda$  and  $\mu$ :

$$\psi_k = \lambda + i\mu_k, \quad k=1-4, \quad . \quad . \quad . \quad (19)$$

or the  $\lambda$ 's and  $\mu$ 's are the real and imaginary parts of the  $\psi$ 's.

### §7. The Energy Tensor.

We evaluate now the energy tensor, and show that we obtain the characteristic difference of energies at transitions. This is reached in wave mechanics by making use of imaginary quantities.

Let us consider only two terms in the expression  $\rho$  in (11), as the other terms give similar results.

For the case of transitions the terms  $\phi_1^2 + \phi_2^2$  in  $\rho$  become

$$\phi_1 \phi_1^1 + \phi_2 \phi_2^1, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where  $\phi$  and  $\phi^1$  belong to different states.



Inserting in (20) the values of the  $\phi$ 's from (18) we easily obtain

$$\begin{aligned}\phi_1\phi_1^1 + \phi_2\phi_2^1 &= (\lambda_2\lambda_2^1 + \mu_2\mu_2^1) \cos(\alpha - \alpha^1) \\ &\quad + (\lambda_2\mu_2^1 - \mu_2\lambda_2^1) \sin(\alpha - \alpha^1) \\ \alpha^1 &= \frac{2\pi}{h}(mcx_5 - W^1t), \quad . \quad . \quad . \quad (21)\end{aligned}$$

and hence

$$\alpha - \alpha^1 = \frac{2\pi}{h}(W^1 - W)t. \quad . \quad . \quad . \quad (22)$$

This is the correct expression for the energies of transitions. As we see, the five-dimensional term  $mcx_5$  drops out from the energy tensor.

It can be easily shown that our energy tensor is identical with Dirac's

### §8. *The Hydrogen Atom.*

We consider now the case of the hydrogen atom, in order to give an instance of a certain peculiarity inherent in these equations.

It is known that a law of conservation can be derived from the imaginary wave equations, and every solution of these equations satisfies the law of conservation.

Now the position appears to be somewhat different in the case of the real equations. A law of conservation follows also from these equations; it is, however, expressed in a five-dimensional form, which represents a conservation in the usual sense only if the fifth term vanishes.

We have therefore to discard all solutions which do not satisfy the condition

$$\frac{\partial j_5}{\partial x_5} = 0. \quad . \quad . \quad . \quad . \quad (23)$$

Let us now show the bearing of these considerations upon the solution of the problem of the hydrogen atom.

In that case  $A_1 = A_2 = A_3 = 0$ , and a glance at the equations (7) shows that they can be satisfied by assuming

$$\left. \begin{aligned}\phi_1, \phi_2, \phi_3, \phi_4 &\sim \sin \frac{2\pi}{h}(mcx_5 - Wt), \\ \phi_5, \phi_6, \phi_7, \phi_8 &\sim \cos \frac{2\pi}{h}(mcx_5 - Wt).\end{aligned}\right\} \quad . \quad (24)$$

Now, evaluating the energy tensor for this solution we obtain that

$$j_5 \sim \sin \frac{2\pi}{h} (mcx_5 - W_1 t) \cos \frac{2\pi}{h} (mcx_5 - W_2 t). \quad (25)$$

Thus the fifth dimension does not drop out; we do not obtain the difference of energies at transitions.

As in this case, however,  $\frac{\partial j_5}{\partial x_5} \neq 0$ , we have to conclude that the solution (24) does not represent a possible physical state.

Let us now give briefly the correct solution for this case. Dirac's equations have been rigorously solved for the hydrogen atom by Prof. Darwin\*. We make use of Darwin's results.

The functions  $\psi$ 's have the following expressions (Darwin's equations 7.4):—

$$\left. \begin{aligned} \psi_1 &= -iF_k R_{k+1}^u [\cos u\phi + i \sin u\phi], \\ \psi_2 &= -iF_k R_{k+1}^{u+1} [\cos (u+1)\phi + i \sin (u+1)\phi], \\ \psi_3 &= (k+u+1)G_k R_k^u [\cos u\phi + i \sin u\phi], \\ \psi_4 &= (-k+u)G_k R_k^{u+1} [\cos (u+1)\phi + i \sin (u+1)\phi], \end{aligned} \right\} \quad (26)$$

where  $F_k$  and  $G_k$  are certain functions of  $r$ , and

$$R_k^u = (k-u)! \sin^u \theta \left( \frac{d}{d \cos \theta} \right)^{k+u} \frac{(\cos^2 \theta - 1)^k}{2^k \cdot k!}.$$

From (26) and (19) we obtain the values of  $\lambda$  and  $\mu$ , and inserting the obtained expressions of  $\lambda$  and  $\mu$  in (18) we get the required solutions of our equations.

So, for instance,

$$\lambda_1 = F_k R_{k+1}^u \sin u\phi, \quad \mu_1 = F_k R_{k+k}^u \cos u\phi;$$

hence

$$\phi_3 = F_k R_{k+1}^u \cos \left[ u\phi + \frac{2\pi}{h} (mcx_5 - Wt) \right],$$

$$\phi_4 = F_k R_{k+1}^u \sin \left[ u\phi + \frac{2\pi}{h} (mcx_5 - Wt) \right].$$

### §9. The Wave Equations for Positive Particles.

Two difficulties, as Dirac† has pointed out, are inherent in the relativity wave equations.

\* Proc. Roy. Soc. A, cxviii. p. 658.

† Proc. Roy. Soc. A, cxvii. p. 610.

(a) They have twice as many solutions as appear to be necessary. The solutions can be schematically represented as

$$\left. \begin{array}{ll} (1) \psi e^{-\frac{2\pi i}{\hbar} Wt}, & \bar{\psi} e^{\frac{2\pi i}{\hbar} Wt}, \\ (2) \psi e^{\frac{2\pi i}{\hbar} Wt}, & \bar{\psi} e^{-\frac{2\pi i}{\hbar} Wt}, \end{array} \right\} \quad . \quad . \quad (27)$$

where  $\psi$  stands for all four functions and  $\bar{\psi}$  is the conjugate of  $\psi$ .

The second set of solutions is associated with negative kinetic energy.

The appearance of negative energy is inherent in any relativity theory. It appears also in the classical theory, but there the kinetic energy changes continuously, and, as it is initially positive, it cannot become negative.

In the quantum theory discontinuous transitions are possible, and it is therefore not easy to separate these two sets of solutions.

Schrödinger\*, however, has recently suggested how to separate the positive and negative solutions.

(b) The relativity imaginary equations have another difficulty; they are valid both for electrons and protons. It can be shown that the conjugates of (14) are equivalent to the same equations where  $e$  is changed into  $-e$ .

Let us elucidate this point by considering the conjugate of the fourth equation (14). It is equal to

$$\left( -\frac{\hbar}{2\pi i c} \frac{\partial}{\partial t} - \frac{e}{c} V + mc \right) \bar{\psi}_4 + \left[ \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial x} - \frac{e}{c} A_1 \right) - i \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial y} - \frac{e}{c} A_2 \right) \right] \bar{\psi}_1 - \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial z} - \frac{e}{c} A_3 \right) \bar{\psi}_2 = 0. \quad (28)$$

We now consider the first equation for a positive particle; we have to change  $e$  into  $-e$ , and we obtain

$$\left( -\frac{\hbar}{2\pi i c} \frac{\partial}{\partial t} - \frac{e}{c} V + mc \right) \psi_1 + \left[ \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial x} - \frac{e}{c} A_1 \right) - i \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial y} - \frac{e}{c} A_2 \right) \right] \psi_4 + \left( \frac{\hbar}{2\pi i} \frac{\partial}{\partial z} - \frac{e}{c} A_3 \right) \psi_3 = 0. \quad (29)$$

Comparing (29) with (28) we find that

$$\begin{array}{l} \psi_1^+, \psi_2^+, \psi_3^+, \psi_4^+ \\ \text{are equivalent to} \\ \bar{\psi}_4, -\bar{\psi}_3, -\bar{\psi}_2, \bar{\psi}_1, \end{array}$$

\* *Berliner Berichte*, p. 63 (1931).

or the equations for the proton are equivalent to the conjugate equations for an electron.

(c) Let us now consider the case of the real equations. Instead of Dirac's four complex functions we have eight real ones, with the corresponding positive and negative solutions :—

$$\left. \begin{aligned} \phi &\sim \frac{\sin}{\cos} \left[ \omega + \frac{2\pi}{h} (mcx_5 - Wt), \right] \\ \phi &\sim \frac{\sin}{\cos} \left[ \omega + \frac{2\pi}{h} (mcx_5 + Wt), \right] \end{aligned} \right\} \quad \dots \quad (30)$$

and

$$\left. \begin{aligned} \phi &\sim \frac{\sin}{\cos} \left[ \omega - \frac{2\pi}{h} (mcx_5 - Wt), \right] \\ \phi &\sim \frac{\sin}{\cos} \left[ \omega - \frac{2\pi}{h} (mcx_5 + Wt), \right] \end{aligned} \right\} \quad \dots \quad (31)$$

where (30) relates to an electron and (31) to a proton;  $\omega$  is a function of the space variables. We see that not only the equations but also the solutions are different for electrons and protons.

Dirac\* has suggested that the negative solutions of an electron could be associated with a proton.

As we see from (30) and (31) this interpretation of negative solutions cannot be justified in our case because the negative solutions of (30) have a different form from (31).

To pass from (30) to (31) we have to change the sign not of  $W$ , but of  $m$ ; this, however, is equivalent in our equations to changing the sign of  $e$ .

#### §10. *On the Meaning of the Fifth Dimension.*

It is known that the idea of the fifth dimension was advanced by Kaluza in order to bring about the welding of gravitation and the electromagnetic field; but this conception appears to be very useful in wave-mechanics; the latter gives us a definite interpretation of the fifth coordinate.

An easy way of introducing the fifth dimension is to follow the same procedure as in the case of four dimensions.

As it is known the four-dimensional principle of relativity is based upon the law of constancy of velocity of light

\* Proc. Roy. Soc. A, cxxvi, p. 360 (1930).

propagation. If  $c$  is the velocity of light, the transformation of coordinates has to leave invariant the expression

$$\frac{ds}{dt} = c, \quad . \quad . \quad . \quad . \quad . \quad (32)$$

or

$$dx^2 + dy^2 + dz^2 - c^2 dt^2 = 0; \quad . \quad . \quad . \quad . \quad (33)$$

this leads to Lorentz's transformations.

In the case of five dimensions we start from the fundamental equation of the quantum theory,

$$h\nu = E. \quad . \quad . \quad . \quad . \quad . \quad (34)$$

As de Broglie has pointed out, the transformation of this equation for moving systems does not conform with the usual principle of relativity; this led him to the wave conception of an electron.

Let us give a metrical representation of the equation (34). We have

$$h\nu = \frac{m_0 c^2}{\sqrt{1 - \frac{v^2}{c^2}}} = \frac{m_0 c^2 dt}{\sqrt{dt^2 - \frac{dx^2 + dy^2 + dz^2}{c^2}}}. \quad . \quad (35)$$

Let

$$\frac{m_0 c^2}{h} = \nu_0 = \frac{1}{T_0}, \quad \nu = \frac{1}{T}; \quad . \quad . \quad . \quad (36)$$

we find from (35)

$$c^2 dt^2 - dx^2 - dy^2 - dz^2 - dx_5^2 = 0, \quad . \quad . \quad . \quad (37)$$

where

$$dx_5 = \frac{cT}{T_0} dt, \quad . \quad . \quad . \quad . \quad . \quad (38)$$

or Planck's frequency condition, applied to an electron in four dimensions, can be considered as a "wave" in a five-dimensional space. From (38) we see that the fifth coordinate describes the periodic phenomenon associated with energy. From (37) we obtain the law of transformation for the fifth coordinate; it is invariant with respect to Lorentz's transformations.

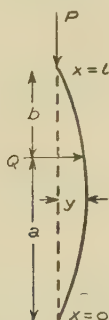
I wish to express my thanks to Prof. Darwin for invaluable criticism of this paper and for many useful suggestions.

LXXVIII. *The Bending of Columns of Varying Cross-section.*—III. By J. A. WILCKEN, B.Sc., Ph.D., Lecturer in Electrical Engineering at Armstrong College, Newcastle-upon-Tyne\*.

IN previous papers† the theory of tapering columns has been developed, as far as it concerns loads acting in a longitudinal sense, whether in the axis or eccentrically. Two types of columns have been discussed, specified as “straight tapering” or “bulging.”

The case of a combined longitudinal and transverse load is important in all structures subject to wind pressure. In a transmission line for electric power any support may be loaded obliquely at times, due to wind effect on conductors and on the mast itself, and where the horizontal trajectory

Fig. 1.



of the line is curved the mast is always subject to a transverse pull.

The following investigation deals with some type of loading that may occur under these circumstances. We consider the transverse load represented by a single force  $Q$ , acting at a given point of the column, in addition to the usual axial thrust  $P$ .

(A)—*A column simply supported at both ends.* The equations of bending moments are, in the usual notation,

$$EI \frac{d^2y}{dx^2} + Py + Qbx/l = 0 \text{ for } a > x > 0, \dots \quad (63)$$

$$EI \frac{d^2y}{dx^2} + Py + Qa(1-x/l) = 0 \text{ for } l > x > a, \dots \quad (64)$$

\* Communicated by the Author.

† Phil. Mag. iii. p. 418, *ibid.* p. 1065 (1927).



with the boundary conditions  $y|_0 = y|_l = 0$ , and subject to the conditions of continuity involving equality of deflexions and curvature at  $x = a$

(i.) In case of a straight tapering column, specified by  $P/EI = (\alpha + \beta x)^{-4}$ , the equations integrate into

$$\left. \begin{aligned} y &= -\frac{Q}{P} bx/l + A(\alpha + \beta x) \sin(\chi_0 - \chi) \\ \text{and} \quad y &= -\frac{Q}{P} a(1 - x/l) + B(\alpha + \beta x) \sin(\chi - \chi_1) \end{aligned} \right\} \quad (65)$$

respectively, where

$$\chi = (\alpha\beta + \beta^2 x)^{-1}, \quad \chi|_0 = \chi_0, \quad \text{and} \quad \chi|_l = \chi_1.$$

Writing also  $\chi|_a = \chi'$ , the conditions of continuity lead to

$$A \sin(\chi_0 - \chi') = B \sin(\chi' - \chi_1).$$

$$A \cos(\chi_0 - \chi') + B \cos(\chi' - \chi_1) = \frac{Q}{P} (\alpha + \beta a);$$

$$\therefore A = \frac{Q}{P} (\alpha + \beta a) \sin(\chi' - \chi_1)$$

$$\operatorname{cosec}(\chi_0 - \chi_1),$$

$$B = \frac{Q}{P} (\alpha + \beta a) \sin(\chi_0 - \chi')$$

$$\operatorname{cosec}(\chi_0 - \chi_1).$$

The quantity  $\chi_0 - \chi_1 = l/\alpha(\alpha + \beta l)$ , which for an axially loaded column of this type becomes equal to  $\pi$  for the "crippling load," we shall denote by  $\lambda$ , and write

$$\chi_0 - \chi = r\lambda,$$

$$\chi_0 - \chi' = s\lambda.$$

Defining, as before (*l.c.*), the taper-ratio  $\rho$  by

$$\alpha + \beta l = \rho\alpha,$$

and putting

$$\alpha + \beta x = \alpha\xi = \alpha\rho x/rl,$$

$$\alpha + \beta a = \alpha\xi' = \alpha\rho a/sl,$$

and substituting in (65), we find, after reduction,

$$\left. \begin{aligned} y &= \frac{Q}{P} (bx/l) \left\{ \frac{\sin(1-s)\lambda \sin r\lambda}{r(1-s)\lambda \sin \lambda} - 1 \right\} \text{ for } a > x > 0, \\ y &= \frac{Q}{P} a(1-x/l) \left\{ \frac{\sin s\lambda \sin(1-r)\lambda}{s(1-r)\lambda \sin \lambda} - 1 \right\} \text{ for } l > x > a, \end{aligned} \right\} \quad (66)$$

and the bending moments thus become

$$\left. \begin{aligned} M &= Q(bx/l) \frac{\sin(1-s)\lambda \sin r\lambda}{r(1-s)\lambda \sin \lambda} \text{ for } a > x > 0, \\ M &= Q\alpha(1-x/l) \frac{\sin s\lambda \sin(1-r)\lambda}{s(1-r)\lambda \sin \lambda} \text{ for } l > x > \alpha. \end{aligned} \right\} \quad (67)$$

When the column is uniform, *i. e.*, when  $\rho=1$ , we have  $r=x/l$ ,  $s=a/l$ ,  $\xi=1$ , and the bending moments become

$$\begin{aligned} M &= Ql \frac{\sin(b\lambda/l) \sin(x\lambda/l)}{\lambda \sin \lambda} \text{ for } a > x > 0, \\ M &= Ql \frac{\sin(a\lambda/l) \sin\{(l-x)\lambda/l\}}{\lambda \sin \lambda} \text{ for } l > x > a, \end{aligned}$$

in agreement with the known formulæ.

(ii.) Considering the "bulging" type of column, specified by  $P/EI=(\alpha+\beta x)^{-2}$ , the solution to the fundamental equations (63) and (64) are written

$$y = -\frac{P}{Q}(bx/l) + A(\alpha+\beta x)^{1/2} \sin(\chi_0 - \chi),$$

and

$$y = -\frac{Q}{P}\alpha(1-x/l) + B(\alpha+\beta x)^{1/2} \sin(\chi - \chi_1),$$

respectively, where

$$\chi = \mu \log(\alpha + \beta x), \quad \mu = \sqrt{\beta^{-2} - \frac{1}{4}}.$$

Writing now

$$\chi_0 - \chi_1 = -\mu \log \rho = \lambda,$$

where  $\lambda$  has the same meaning as above, and using the same notation as under (i.), we find, after reduction,

$$\left. \begin{aligned} y &= \frac{Q}{P} \{ \alpha \sqrt{\xi \xi'} \sin(1-s)\lambda \sin r\lambda \operatorname{cosec} \lambda - bx/l \} \\ &\hspace{15em} \text{for } a > x > 0, \\ y &= \frac{Q}{P} \{ \alpha \sqrt{\xi \xi'} \sin s\lambda \sin(1-r)\lambda \operatorname{cosec} \lambda - \alpha(1-x/l) \} \\ &\hspace{15em} \text{for } l > x > \alpha, \end{aligned} \right\} \quad \dots \quad (68)$$

and so the bending moments become

$$\left. \begin{aligned} M &= Q\alpha \sqrt{\xi \xi'} \sin(1-s)\lambda \sin r\lambda \operatorname{cosec} \lambda \text{ for } a > x > 0, \\ M &= Q\alpha \sqrt{\xi \xi'} \sin s\lambda \sin(1-r)\lambda \operatorname{cosec} \lambda \text{ for } l > x > \alpha. \end{aligned} \right\} \quad \dots \quad (69)$$

The uniform column is to be considered a special case also of this type, as a simple calculation will show.

If the longitudinal thrust  $P$  does not act in direction of the axis, but at a distance  $f$  from it, there will be an additional deflexion as found above (*l. c.* p. 1066), namely,

$$y' = f \left\{ 1 - \xi \left( \cos r\lambda + \frac{1/\rho - \cos \lambda}{\sin \lambda} \sin r\lambda \right) \right\}$$

for the straight tapering column, and

$$y' = f \left\{ 1 - \sqrt{\xi} \left( \cos r\lambda + \frac{\sqrt{1/\rho - \cos \lambda}}{\sin \lambda} \sin r\lambda \right) \right\}$$

for type (ii.); and, correspondingly, additional bending moments, due to the eccentricity of the load. The fact that these values are additively superposed on those due to the load  $Q$  is inherent in the linear character of the fundamental differential equations. An easy calculation based on the complete equations will bear out this statement.

As would be expected, the transverse load  $Q$  always causes a definite deflexion and a finite bending moment whether  $P$  is axial or not, and this bending moment is directly proportional to  $Q$  and depends in a more intricate manner on  $P$  through the quantity denoted  $\lambda$ , which may be written  $\pi \sqrt{P/P_E}$ ,  $P_E$  being the Eulerian crippling load on an axially loaded column. If  $Q$  becomes vanishingly small, the bending moment decreases indefinitely unless at the same time  $\lambda \rightarrow \pi$ , *i. e.*, unless  $P$  approaches the crippling value.

(B)—*A column built in at one end and free at the other end.* The bending moments in the two portions of the column are given by the equations

$$\left. \begin{aligned} EI \frac{d^2 y}{dx^2} + P(y-h) + Q(x-a) &= 0 \text{ for } a > x > 0, \\ EI \frac{d^2 y}{dx^2} + P(y-h) &= 0 \text{ for } l > x > a, \end{aligned} \right\} \quad (70)$$

with the boundary conditions  $y^0 = 0 = \frac{dy^0}{dx}$ ,  $y^l = h$ , and the conditions of continuity of deflexion and curvature at  $x = a$ .

(i.) If the column is of the type  $(\alpha + \beta x)^{-4} = P/EI$ , the solutions to the above equations are written

$$y = h + \frac{Q}{P} (a - x) + (\alpha + \beta x) (A_1 \cos \chi + A_2 \sin \chi)$$

and  $y = h + (\alpha + \beta x) (B_1 \cos \chi + B_2 \sin \chi)$  respectively.

The boundary conditions are equivalent to

$$A_1 \cos \chi_0 + A_2 \sin \chi_0 = -\frac{1}{\alpha} (h + aQ/P),$$

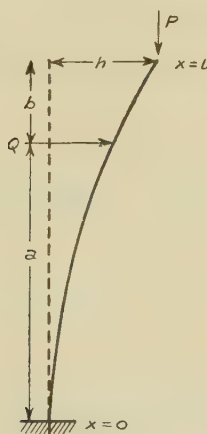
$$A_1(\beta \cos \chi_0 + \frac{1}{\alpha} \sin \chi_0) + A_2(\beta \sin \chi_0 - \frac{1}{\alpha} \cos \chi_0) = Q/P,$$

leading to

$$A_1 = -\frac{1}{\alpha} (h + aQ/P) \cos \chi_0 + \{\beta h + (\alpha + \beta a)Q/P\} \sin \chi_0,$$

$$A_2 = -\frac{1}{\alpha} (h + aQ/P) \sin \chi_0 - \{\beta h + (\alpha + \beta a)Q/P\} \cos \chi_0.$$

Fig. 2.



Substituting these values for the integration constants, we find, for the deflexion below  $Q$ ,

$$y = h + (a-x)Q/P + (\alpha + \beta x) \left\{ -\frac{1}{\alpha} (h + aQ/P) \cos (\chi_0 - \chi) + [\beta h + (\alpha + \beta a)Q/P] \sin (\chi_0 - \chi) \right\},$$

and introducing the notation as defined above, and rearranging,

$$y = h \left\{ 1 - \xi \left( \frac{1/\rho - 1}{\lambda} \sin r\lambda + \cos r\lambda \right) \right\} + \frac{Q}{P} \left\{ a - x + a\xi \left( \frac{1}{s\lambda} \sin r\lambda - \cos r\lambda \right) \right\} \text{ for } a > x > 0. \quad (71)$$

To determine the constants  $B_1$  and  $B_2$  we have the conditions

$$B_1 \cos \chi_1 + B_2 \sin \chi_1 = 0 \text{ for } x=l,$$

and

$$\left. \begin{aligned} (A_1 - B_1) \cos \chi' + (A_2 - B_2) \sin \chi' &= 0, \\ (A_1 - B_1) \sin \chi' - (A_2 - B_2) \cos \chi' &= (\alpha + \beta a) Q/P, \end{aligned} \right\} \text{ at } x=a.$$

These give

$$B_1 = A_1 - (\alpha + \beta a) \frac{Q}{P} \sin \chi',$$

$$B_2 = A_2 + (\alpha + \beta a) \frac{Q}{P} \cos \chi',$$

whence the deflexion above  $Q$  becomes

$$y = h \left\{ 1 - \xi \left( \frac{1/\rho - 1}{\lambda} \sin r\lambda + \cos r\lambda \right) \right\} \\ + a\xi \frac{Q}{P} \left\{ \frac{1}{s\lambda} [\sin r\lambda - \sin(r-s)\lambda] - \cos r\lambda \right\} \text{ for } l > x > a. \quad (72)$$

The bending moments now are

$$\left. \begin{aligned} M_1 &= Ph\xi \left( \cos r\lambda + \frac{1/\rho - 1}{\lambda} \sin r\lambda \right) + Qa\xi \left( \cos r\lambda - \frac{1}{s\lambda} \sin r\lambda \right) \\ \text{and} \\ M_2 &= M_1 - Q \frac{a\xi}{s\lambda} \sin(r-s)\lambda \text{ for } l > x > a. \end{aligned} \right\} \text{ for } a > x > 0, \quad (73)$$

The deflexion at the top is obtained putting  $\xi = \rho$  and  $r=1$  in the expression for  $y|^{l>x>a}$ ,

$$y|^{l>x>a} = h \left\{ 1 - \rho \left( \frac{1/\rho - 1}{\lambda} \sin \lambda + \cos \lambda \right) \right\} \\ + a\rho \frac{Q}{P} \left\{ \frac{1}{s\lambda} (\sin \lambda - \sin(1-s)\lambda) - \cos \lambda \right\}$$

leading to

$$h = a \frac{Q}{P} \frac{\frac{1}{s\lambda} \{ \sin \lambda - \sin(1-s)\lambda \} - \cos \lambda}{\frac{1/\rho - 1}{\lambda} \sin \lambda + \cos \lambda}. \quad (74)$$

If the transverse load  $Q$  act at the top  $a=l$  and  $s=1$ , and we have

$$h = l \frac{Q}{P} \frac{1 - \lambda \cot \lambda}{1/\rho - 1 + \lambda \cot \lambda}. \quad (75)$$

These expressions become infinite for  $\lambda \cot \lambda = 1 - 1/\rho$  unless at the same time  $Q$  becomes infinitely small. The meaning of this is that when the vertical load  $P$  approaches a certain value, such that  $\lambda \cot \lambda \rightarrow 1 - 1/\rho$ , an infinitely small transverse force is sufficient to cause deflexion. The limiting value of the vertical load is seen to agree with the "crippling load" previously defined (*l. c.* p. 424).

(ii.) For a column of the bulging type, as specified by  $P/EI = (\alpha + \beta x)^{-2}$ , the solutions to the equation (70) are written

$$y = h + (a - x)Q/P + \sqrt{\alpha + \beta x}(A_1 \cos \chi + A_2 \sin \chi)$$

and

$$y = h + \sqrt{\alpha + \beta x}(B_1 \cos \chi + B_2 \sin \chi)$$

respectively, with

$$\chi = \mu \log(\alpha + \beta x).$$

The conditions at  $x=0$  and  $x=l$  lead to

$$A_1 \cos \chi_0 + A_2 \sin \chi_0 = -\frac{1}{\sqrt{\alpha}}(h + aQ/P),$$

$$A_1 \sin \chi_0 - A_2 \cos \chi_0 = -h/2\mu\sqrt{\alpha} - (Q/2\mu P)(2\sqrt{\alpha}/\beta + a/\sqrt{\alpha}),$$

from which we find

$$A_1 = -\frac{h}{\sqrt{\alpha}}\left(\cos \chi_0 + \frac{1}{2\mu} \sin \chi_0\right) - \frac{Q}{P} \left\{ \frac{a}{\sqrt{\alpha}}\left(\cos \chi_0 + \frac{1}{2\mu} \sin \chi_0\right) + \frac{\sqrt{\alpha}}{\mu\beta} \sin \chi_0 \right\},$$

$$A_2 = -\frac{h}{\sqrt{\alpha}}\left(\sin \chi_0 - \frac{1}{2\mu} \cos \chi_0\right) - \frac{Q}{P} \left\{ \frac{a}{\sqrt{\alpha}}\left(\sin \chi_0 - \frac{1}{2\mu} \cos \chi_0\right) - \frac{\sqrt{\alpha}}{\mu\beta} \cos \chi_0 \right\}.$$

Substituting above, we find for the deflexion below  $Q$

$$y = h \left\{ 1 - \sqrt{\xi} \left( \cos r\lambda + \frac{1}{2\mu} \sin r\lambda \right) \right\} + \frac{Q}{P} \left\{ a - x - \sqrt{\xi} \left[ a \left( \cos r\lambda + \frac{1}{2\mu} \sin r\lambda \right) + \frac{l}{\mu(\rho - 1)} \sin r\lambda \right] \right\} \dots \quad (76)$$

To determine the constants  $B_1$  and  $B_2$  we have

$$B_1 \cos \chi_1 + B_2 \sin \chi_1 = 0,$$



and the continuity conditions

$$(A_1 - B_1) \cos \chi' + (A_2 - B_2) \sin \chi' = 0,$$

$$(A_1 - B_1) \sin \chi' - (A_2 - B_2) \cos \chi' = \frac{Q}{P} \cdot \frac{\sqrt{\alpha + \beta a}}{\mu \beta},$$

and from these we find

$$B_1 = A_1 - \frac{Q}{P} \frac{\sqrt{\alpha + \beta a}}{\mu \beta} \sin \chi',$$

$$B_2 = A_2 + \frac{Q}{P} \frac{\sqrt{\alpha + \beta a}}{\mu \beta} \cos \chi'.$$

The deflexion above Q is thus expressed by

$$y = h \left\{ 1 - \sqrt{\xi} \left( \cos r\lambda + \frac{1}{2\mu} \sin r\lambda \right) \right\} \\ + \frac{Q}{P} \sqrt{\xi} \left\{ \frac{l}{\mu(1-\rho)} (\sin r\lambda + \sqrt{\xi'} \sin (r-s)\lambda) \right. \\ \left. - a \left( \cos r\lambda + \frac{1}{2\mu} \sin r\lambda \right) \right\}. \quad (77)$$

The bending moments for the two portions of the column become

$$M_1 = Ph \sqrt{\xi} \left( \cos r\lambda + \frac{1}{2\mu} \sin r\lambda \right) \\ + Q \sqrt{\xi} \left\{ a \left( \cos r\lambda + \frac{1}{2\mu} \sin r\lambda \right) - \frac{l}{\mu(1-\rho)} \sin r\lambda \right\} \\ \text{for } a > x > l, \quad . \quad . \quad . \quad (78)$$

$$\text{and } M_2 = M_1 - Q \sqrt{\xi} \frac{l \sqrt{\xi'}}{\mu(1-\rho)} \sin (r-s)\lambda \text{ for } l > x > a.$$

The deflexion at the top is found as before,

$$h = \frac{Q}{P} \cdot \left\{ \frac{2l}{1-\rho} \cdot \frac{\sin \lambda + \sqrt{\xi'} \sin (1-s)\lambda}{\sin \lambda + 2\mu \cos \lambda} - a \right\}, \quad (79)$$

and if Q acts at the top this becomes

$$h = \frac{Q}{P} l \left\{ \frac{2}{(1-\rho)(1+2\mu \cot \lambda)} - 1 \right\}. \quad . \quad . \quad (80)$$

The two expressions for  $h$  show, as above, that if  $P$  approaches the crippling value, defined by  $\cot \lambda \rightarrow -1/2\mu$  or  $(\mu \log \rho) \cot (\mu \log \rho) \rightarrow \frac{1}{2} \log \rho$ , an infinitely small transverse force will cause a finite bending moment.

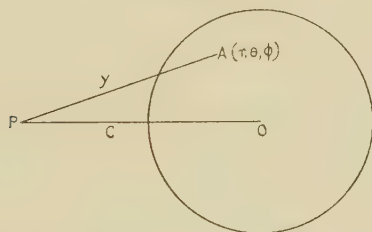
LXXIX. *The Cohesive Force between Solid Surfaces and the Surface Energy of Solids.* By R. S. BRADLEY, M.A.\*

THE cohesion between quartz fibres and between equal glass spheres has been described by Tomlinson<sup>(1)</sup>. The cohesive force was measured by the bending of the fibres. In this paper an improved method is described for measuring the cohesive force between unequal spheres in geometrical contact, as it is difficult to get spheres exactly equal in radii, and the bearing of the measurements on the surface energy of solids is discussed.

1. *Theoretical.*—*The Cohesive Force between Two Spheres.*

The cohesive force between two spheres may be found on the assumption that two molecules of the solid, whose centres are a distance  $x$  apart, attract one another with a force

Fig. 1.



$\frac{\lambda}{x^n}$ , where  $n$  is an integer. London and Eisenschitz<sup>(2)</sup> and Slater<sup>(3)</sup> have shown by wave mechanics that the predominant term in the attraction between molecules depends on the inverse seventh power of the distance at sufficient distances. London points out that, although this force is electrical in origin the attraction between two molecules is independent of the presence of a third, as with the gravitational force. This is exactly the type of force considered below. In particular surface molecules will attract with the same law as those in the interior.

The force between two spheres may be calculated rigorously as follows:—As a preliminary the potential of a single molecule,  $P$  in fig. 1, due to a solid sphere of centre  $O$ , will first be considered. The coordinates of any point  $A$  on the surface are  $r, \theta, \phi$ .

\* Communicated by the Author.

Let there be  $q$  attracting molecules per unit volume of the solid sphere. The potential of a molecule at P due to a polar element of volume  $r^2 \sin \theta \cdot d\theta \cdot d\phi \cdot dr$  at A will be

$$-\frac{q\lambda r^2 \sin \theta d\theta d\phi dr}{(n-1) \cdot y^{n-1}},$$

where  $PA=y$ . Hence the potential at P due to a spherical shell is

$$-\frac{r^2 q \lambda dr}{(n-1)} \iiint \frac{\sin \theta d\theta d\phi}{y^{n-1}}.$$

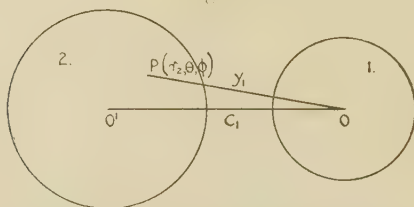
Since  $y^2 = c^2 + r^2 - 2cr \cos \theta$ , where  $PO=c$ , this becomes

$$-\frac{2\pi r q \lambda dr}{c(n-1)} \int_{c-r}^{c+r} \frac{dy}{y^{n-2}} = \frac{2\pi q \lambda dr}{c(n-1)(n-3)} \left[ \frac{r}{(c+r)^{n-3}} - \frac{r}{(c-r)^{n-3}} \right].$$

On integrating with respect to  $r$  between the limits  $r$  and 0 we get the potential at P due to a solid sphere. This is

$$\frac{2\pi q \lambda}{c(n-1)(n-3)} \left[ \frac{-1}{(n-5)(c+r)^{n-5}} + \frac{c}{(n-4)(c+r)^{n-4}} \right. \\ \left. + \frac{1}{(n-5)(c-r)^{n-5}} - \frac{c}{(n-4)(c-r)^{n-4}} \right].$$

Fig. 2.



We now consider the mutual potential of two solid spheres. In fig. 2 the potential of a molecule at P due to a solid sphere of centre O, radius  $r_1$ , is obtained from the last expression by putting  $r=r_1$ ,  $c=y_1$ . Hence, as before, the mutual potential of a polar element of volume  $r_2^2 \sin \theta d\theta d\phi dr_2$  at P and the sphere 1 is

$$\frac{2\pi q^2 \lambda r_2^2}{(n-1)(n-3)} \sin \theta d\theta d\phi dr_2 \left[ -\frac{1}{(n-5)y_1(y_1+r_1)^{n-5}} \right. \\ \left. + \frac{1}{(n-4)(y_1+r_1)^{n-4}} + \frac{1}{(n-5)y_1(y_1-r_1)^{n-5}} \right. \\ \left. - \frac{1}{(n-4)(y_1-r_1)^{n-4}} \right], \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where  $r_2$  is the radius of the second sphere.

Since  $y_1^2 = c_1^2 + r_2^2 - 2c_1r_2 \cos \theta$ , where  $c_1 = O O'$ , the mutual potential of a spherical shell of radius  $r_2$  and the solid sphere 1, is

$$\frac{4\pi^2 q^2 \lambda r_2 dr_2}{(n-1)(n-3)c_1} \int_{c_1-r_2}^{c_1+r_2} y_1 \cdot X \cdot dy, \quad \dots \quad (2)$$

where  $X$  is the expression in square brackets in (1). The integral in (2) is easily evaluated to be

$$\frac{1}{(n-4)(n-5)} \left[ \frac{1}{(n-6)(y_1+r_1)^{n-6}} + \frac{r_1}{(y_1+r_1)^{n-5}} - \frac{1}{(n-6)(y_1-r_1)^{n-6}} + \frac{r_1}{(y_1-r_1)^{n-5}} \right]_{c_1-r_2}^{c_1+r_2}.$$

To obtain the mutual potential of the two solid spheres (2) is now integrated with  $r_2$  as variable, between the limits  $r_2$  and 0. This gives the result

$$\frac{4\pi^2 q^2 \lambda}{(n-1)(n-3)(n-4)(n-5)} \frac{Y}{c_1},$$

where  $Y$  is equal to

$$\begin{aligned} & - \frac{1}{(n-6)(n-8)(c_1+r_1+r_2)^{n-8}} + \frac{(c_1+r_1)}{(n-6)(n-7)(c_1+r_1+r_2)^{n-7}} \\ & + \frac{1}{(n-6)(n-8)(c_1-r_1+r_2)^{n-8}} - \frac{(c_1-r_1)}{(n-6)(n-7)(c_1-r_1+r_2)^{n-7}} \\ & - \frac{r_1}{(n-7)(c_1+r_1+r_2)^{n-7}} + \frac{r_1(c_1+r_1)}{(n-6)(c_1+r_1+r_2)^{n-6}} \\ & - \frac{r_1}{(n-7)(c_1-r_1+r_2)^{n-7}} + \frac{r_1(c_1-r_1)}{(n-6)(c_1-r_1+r_2)^{n-6}} \\ & - \frac{(c_1+r_1)}{(n-6)(n-7)(c_1+r_1-r_2)^{n-7}} + \frac{1}{(n-6)(n-8)(c_1+r_1-r_2)^{n-8}} \\ & + \frac{(c_1-r_1)}{(n-6)(n-7)(c_1-r_1-r_2)^{n-7}} - \frac{1}{(n-6)(n-8)(c_1-r_1-r_2)^{n-8}} \\ & - \frac{r_1(c_1+r_1)}{(n-6)(c_1+r_1-r_2)^{n-6}} + \frac{r_1}{(n-7)(c_1+r_1-r_2)^{n-7}} \\ & - \frac{r_1(c_1-r_1)}{(n-6)(c_1-r_1-r_2)^{n-6}} + \frac{r_1}{(n-7)(c_1-r_1-r_2)^{n-7}} \quad \dots \quad (3) \end{aligned}$$

This is now differentiated with respect to  $c_1$ , and  $c_1$  is put equal to  $r_1+r_2+d$ , where  $d$  is the nearest distance between

the centres of surface molecules of the spheres. Since the spheres are touching in the experiment,  $d$  is the molecular diameter; hence  $d$  may be neglected compared with  $c_1$ ,  $r_1$ , or  $r_2$ . Therefore only those terms need be included which have  $c_1 - r_1 - r_2$ , i. e.,  $d$ , in the denominator. Other terms are retained in (3) in order to show that the potential can be expressed in a finite form even if this condition is not complied with, and in order to avoid leaving out terms at an early stage in the calculation.

The force between the two spheres, when  $d$  is very small compared with  $r_1$ ,  $r_2$ , and  $c_1$ , is therefore

$$\frac{4\pi^2 q^2 \lambda}{(n-1)(n-3)(n-4)(n-5)} Z,$$

where  $Z$  is given by

$$\begin{aligned} & - \frac{1}{(n-6)} \frac{c_1 - r_1}{c_1 d^{n-6}} + \frac{r_1}{(n-6)(n-7)c_1^2 d^{n-7}} + \frac{1}{(n-6)c_1 d^{n-7}} \\ & + \frac{1}{(n-6)(n-8)c^2 d^{n-8}} + \frac{r_1(c_1 - r_1)}{c_1 d^{n-5}} - \frac{r_1^2}{(n-6)c_1^2 d^{n-6}} \\ & - \frac{r_1}{c_1 d^{n-6}} - \frac{r_1}{(n-7)c_1^2 d^{n-7}}. \end{aligned}$$

Here again only the fifth term is of any importance, as other terms are only approximately  $d^2$ ,  $d^2$ ,  $d^3$  as large. Hence the attraction is

$$\frac{4\pi^2 q^2 \lambda}{(n-1)(n-3)(n-4)(n-5)} \frac{r_1 r_2}{r_1 + r_2} \frac{1}{d^{n-5}} \quad (4)$$

The result (3) holds only when  $n > 8$ . As an inverse seventh power is likely from quantum mechanics, it is interesting to see what result is obtained in this case. Terms containing indices of the power  $n-6$  in  $Y$  remain the same, and, in addition, one must add

$$\begin{aligned} & -(c_1 + r_1) \log \frac{c_1 + r_1 + r_2}{c + r_1} + (c_1 - r_1) \log \frac{c_1 + r_2 - r_1}{c_1 - r_1} \\ & + (c_1 + r_1) \log \frac{c_1 + r_1 - r_2}{c_1 + r_1} - (c_1 - r_1) \log \frac{c_1 - r_1 - r_2}{c_1 - r_1}. \end{aligned}$$

On differentiating  $\frac{Y}{c_1}$  as before with respect to  $c_1$ , the result (4) is again obtained, if  $c_1$ ,  $r_1$ ,  $r_2$  are of the order  $10^{-1}$  cm. and  $d$  is of the order  $10^{-8}$  cm. The same result (4) is obtained if  $n$  is 8.

Expression 4 is symmetrical, as it should be in  $r_1$  and  $r_2$ , and has the correct dimensions, since  $\frac{\lambda}{d}$  is a force.

## 2. The Surface Energy of the Solid.

The measurement of the cohesive force between smooth surfaces provides a new method for finding the surface energy of solids. On the assumption already made for the law of force the total surface energy is <sup>(4)</sup>

$$\frac{\pi q^2 \lambda}{(n-1)(n-3)(n-4)(n-5)} \frac{1}{d^{n-5}}.$$

Let the diameters of the two spheres be  $d_1$  and  $d_2$ . Then the cohesive force between them may be written in the form  $A \frac{d_1 d_2}{d_1 + d_2}$ , where A is a constant independent of the dimensions of the spheres in the region of dimensions considered. Then on the above analysis the surface energy of the solid is

$$\frac{A}{2\pi}.$$

This relation holds, moreover, if a repulsive term is included in the intermolecular force, which will then be of the form

$$\frac{\lambda}{x^n} - \frac{\mu}{x^m}$$

(probably more nearly representing the actual force). It thus appears that the total surface energy may be calculated without having to use accurately plane surfaces in order to measure the cohesion; but owing to the assumptions involved the result can be regarded only as a first approximation. In view, however, of the small amount of experimental work on the surface energy of solids the author feels that the method is of interest. Previous calculations of the surface energy have involved solubility measurements. Antonoff's <sup>(5)</sup> method, which assumes that the surface tension of a solid equals that of a liquid which neither rises nor falls in a capillary tube of the solid has been criticized by Adam <sup>(6)</sup>, who points out that what is measured is the work of adhesion of the liquid to the solid.

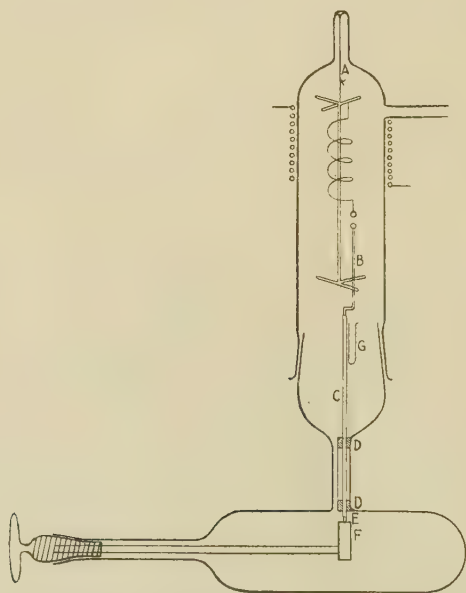
## 3. The Apparatus.

The essential part of the apparatus is shown in fig. 3. One of the spheres is supported by a quartz spiral spring, which is attached to a quartz frame hanging on a hook A. On sliding a glass tube constricted at one point round the spiral spring the base of the frame rests against the constriction, and the spring may be removed. The other sphere is



attached to the rod B, which is waxed, with vacuum wax, into the brass rod C. C slides accurately through two guides D, D, fixed into a brass tube which is waxed to the surrounding glass tube on one side. In this way a gap is left whereby the lower part of the apparatus may be evacuated. On the end of C is fixed a small wheel, which runs on the wheel of the cam F. F is carried by a brass tube waxed to a stopper (made from a ground joint). G is a tube carrying a small amount of radioactive deposit to discharge any electrification. A heating coil may be slid over the two spheres. Apiezon grease was used.

Fig. 3.



When a determination of the cohesive force is to be made the stopper is rotated slowly, so that the two spheres come into contact. On rotating the stopper slowly in the reverse direction the upper sphere is pulled down until separation occurs. The distance between two horizontal tangent planes to the spheres is read on the microscope, and gives a measure of the cohesive force between the two spheres in geometrical contact. When the spheres are allowed to come together a slight flattening occurs at the region of contact, and on pulling the spheres apart by a force acting along their

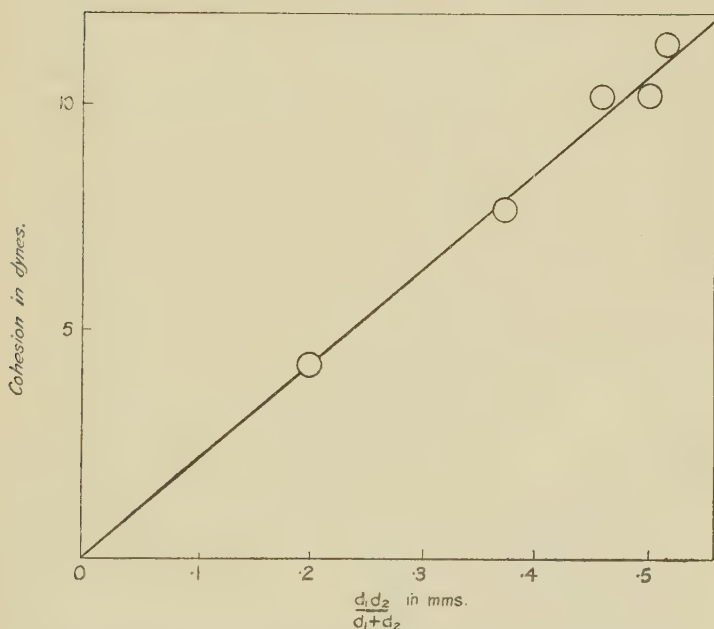
line of centres this flattening will decrease until geometrical contact is reached just before separation.

The spring was calibrated by means of weights made from platinum wire.

#### 4. Results with Quartz Spheres.

The upper quartz sphere was fused to the spiral spring, the lower to the quartz B. The spheres had thin necks, and

Fig. 4.



were then nearly spherical at the portions which came into contact. The spheres were heated to incandescence in an oxy-gas blow-pipe, the apparatus was assembled, and the cohesion measured. A large number of settings were made and the mean taken. A repetition of this procedure gave the same result to within a few per cent. The temperature was about  $15^\circ \text{C}$ .

The results are embodied in fig. 4, which gives the plot of the product of the diameter of the spheres divided by their sum against the cohesive force. A straight line is obtained, which, in agreement with theory, goes through the origin.

The apparatus was evacuated, with the heater on, by means of a mercury-vapour diffusion-pump. The same result was obtained to within the accuracy of the method.

From the straight line the constant  $A$  of section 2 is found to be 212. This corresponds to a surface energy of 33.8 ergs per sq. cm. It is unlikely that a surface film of water would withstand the baking-out adopted, so that the cohesive force is probably a true property of the surface. The fact that the same result was obtained in air as in a vacuum may be due to the squeezing out of adsorbed air molecules from quartz molecules which come nearly into contact, or the gas film may not be removed by baking-out. Consider two surface molecules, one on the surface of each sphere, and the line joining their centres parallel to the line of centres of the two quartz spheres. If the shortest distance between the surface of these surface molecules is  $\Delta$ , then their centres lie on circles of radius  $\left(\frac{d_1 d_2 \Delta}{d_1 + d_2}\right)^{\frac{1}{2}}$ . If  $\Delta$  corresponds to twice the diameter of an adsorbed molecule, say 5 Å.U., and  $\frac{d_1 d_2}{d_1 + d_2}$  is  $5 \times 10^{-1}$  cm., this radius is  $5 \times 10^{-5}$  cm., so that only a small fraction of the surface of the quartz spheres need be desorbed of air molecules.

It is unlikely that the forces measured are due to electrification of the quartz. One would not expect the value of the force between the two spheres to be reproduced after heating the spheres again in the blow-pipe if the results were due to electrification; neither would one expect the force to remain constant with time in the presence of the discharging radioactive deposit. Before starting the work the author repeated Tomlinson's experiment with two fibres carrying quartz spheres. The fibres were drawn out from a quartz rod, which was waxed to a thick-walled glass capillary. The two glass capillaries were inserted through a rubber bung in a bottle, on the bottom of which was a cup containing a little radioactive salt. The glass tubes were bent towards one another until the quartz spheres touched. On bending the tubes away from one another the spheres remained in contact until the fibres had been bent to a certain amount, which did not appear to change for weeks.

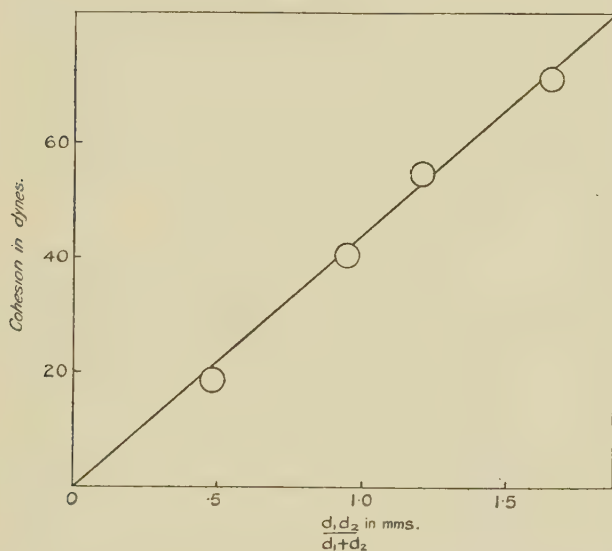
The quartz spheres have cooled from the liquid by becoming increasingly more viscous. As there is presumably no violent discontinuity in this process, the surface of the quartz glass would be expected to be sufficiently smooth. The mean of a large number of determinations was taken in

each case, so that neighbouring points could come into contact, and these means differed, as already stated, by only a few per cent.

### 5. Results with Borate Spheres.

The method is limited to glassy solids, as crystallization is bound to develop large cracks. Glass was considered unsuitable because of its uncertain composition; sodium pyroborate,  $\text{Na}_2\text{B}_4\text{O}_7$ , was therefore tried. The tip of a platinum wire was fused to a small sphere in an oxy-gas

Fig. 5.



flame, and was dipped repeatedly into molten borax, which had been fused until free from bubbles. The blob of borax was manipulated in a small flame to form a sphere attached by a short thin neck to the platinum sphere. The borax did not then crack on cooling. One sphere was hung from a hook on the spiral spring, the platinum wire attached to the other was sealed into the rod B, now of glass.

Results for freshly fused spheres are shown in fig. 5. Here also a straight line is obtained, passing as it should through the origin. The constant A has the value 434, corresponding to a surface energy of 69 ergs per sq. cm. In this case the cohesion sinks in a vacuum to about a third. Very probably, therefore, a water film is responsible for the

cohesion in air, and the removal of this film probably leaves the surface in a rough condition, as one would expect the surface energy of a salt such as pyroborate to be greater than that of quartz. In accordance with this, while dry air had no effect, the cohesion rose on admitting water vapour to the spheres in a vacuum, but no reproducible result could be obtained.

My thanks are due to Mr. Tomlinson and to Professor Lennard-Jones for reading the manuscript in one stage of its preparation.

#### *Summary.*

An expression is obtained for the cohesive force between two unequal spheres in geometrical contact. From the constant in this expression the surface energy of the solid may be computed. Results are obtained in agreement with the theory. The surface energies of freshly fused surfaces of quartz and sodium pyroborate are 33.8 and 69 ergs per sq. cm. In the case of borate spheres, however, the cohesion is probably due to a surface film of water.

#### *References.*

- (1) Tomlinson, *Phil. Mag.* vi. p. 695 (1928); x. p. 541 (1930).
- (2) London and Eisenschitz, *Zeit. f. Physik.* lxx. p. 491 (1930); London, *Zeit. f. Phys. Chem.* B, xi. p. 223 (1930).
- (3) Slater, *Phys. Rev.* xxxvii. p. 682 (1931).
- (4) Bradley, *Phil. Mag.* xi. p. 846 (1931).
- (5) Antonoff, *Phil. Mag.* vii. p. 1258 (1926).
- (6) Adam, *Phil. Mag.* vii. p. 863 (1927).

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#### LXXX. *The Vibrations of Revolving Shafts.*

By DAVID ROBERTSON, *D.Sc., M.I.E.E.\**

IN the *Phil. Mag.* for August 1931 (Suppl.), on pp. 297-311, there appears a paper by Dr. R. C. J. Howland bearing the above title.

The first portion of this paper is based on the inaccurate statements that the assumption of negligible gyrostatic effects gives "equations which are the same relative to axes rotating with the shaft as they would be with respect to fixed axes, except that a field of centrifugal force must be introduced.

\* Communicated by the Author.

It also leads to the result that the motions in any two mutually perpendicular planes through the axis, and revolving with it, are sensibly independent."

These statements take no account of the Coriolis acceleration in the  $y$ -direction which is necessary to change the direction of the  $x$ -velocity as the axes of reference rotate, and to keep the point moving tangentially at the same rate as the reference plane as the distance from the centre of rotation alters because of the  $x$ -velocity; and of the similar acceleration in the  $x$ -direction because of the  $y$ -velocity.

Let the coordinates of the moving point, referred to axes rotating at  $\omega$ , be  $x, y$ ; and to fixed axes which coincide with the rotating axes at zero time be  $x', y'$ . Then, if the rotation is from  $x$  to  $y$ , we have

$$\begin{aligned}x' &= x \cos \omega t - y \sin \omega t, \\ \dot{x}' &= (\dot{x} \cos \omega t - \dot{y} \sin \omega t) - \omega(x \sin \omega t + y \cos \omega t), \\ \ddot{x}' &= (\ddot{x} \cos \omega t - \ddot{y} \sin \omega t) - 2\omega(\dot{x} \sin \omega t + \dot{y} \cos \omega t) \\ &\quad - \omega^2(x \cos \omega t - y \sin \omega t); \end{aligned}$$

with similar expressions for the  $y$ -coordinates.

The first two terms of the right-hand side of the last equation give the component in the fixed  $x$ -direction of the acceleration relative to the rotating axes; the second pair gives that of the Coriolis acceleration, and the last pair that of the centripetal acceleration.

From the above equations it is evident that neither of the statements quoted above from Dr. Howland's paper is correct, and that the conclusions which he draws from them are consequently invalid.

Using stroboscopic vision it is quite easy to demonstrate experimentally that the frequency of vibration of a shaft does not vary with the speed of rotation as required by Dr. Howland's equation (5), but remains sensibly the same as when there is no rotation, so long as the speed is insufficient to produce appreciable gyrostatic effects.

The stroboscopic shutter may be attached to a small motor whose speed is kept constant at that value which makes the vibrating, but not revolving, shaft appear to stand still with a bent form which gradually straightens as the vibration dies away. With a single slot shutter this speed will be found identical with the critical speed of the shaft.

If whilst rotating at any speed the shaft be set into vibration by a blow, its stroboscopic appearance will be the same as when it was not rotating, except for the whirl due



to any want of balance, thus showing that the frequency has not been altered by the rotation.

Near the critical speed the whirl due to unbalance may be too large to permit the vibration to be distinguished from it; but the proof can be extended to this range by attaching the shutter to the motor driving the shaft instead of to a separate motor.

The stroboscope then eliminates, so far as vision is concerned, all periodic motions of the rotation frequency, including the rotation itself, and the other vibrations are seen with their frequency apparently reduced by an amount equal to the speed of the shaft. Within about 200 r.p.m. of the critical speed the apparent frequency of the vibrations set up by a blow can be timed, and their actual frequency determined by allowing for the speed of the shaft. It will again be found to be the same as the critical speed.

In essentials Howland's fallacy is identical with that of Chree\* and of the others who followed him in predicting a critical speed at  $\Omega/\sqrt{2}$ .

This fallacy has been repeatedly exposed, among others by Rodgers on pp. 129-130 of the 1922 paper which Dr. Howland mentions.

There are at least four papers which give measurements of the magnitude of elastic hysteresis, or internal friction, in steel, and one point upon which they do agree is that the forces concerned are *quite independent of the velocity of strain*†.

Thus the assumption that these forces are proportional to the velocity of strain, upon which most of the remainder of Dr. Howland's paper is founded, is contrary to the known facts.

His reference to Filon and Jessop's paper misleads the reader into supposing that these writers have put forward this assumption as one which fairly represents the facts for *all* materials, whereas they state quite the contrary. After mentioning that they tried it for *one* material, they proceed:—"A thorough examination of a number of curves,

\* "The Whirling and Transverse Vibrations of Rotating Shafts," Proc. Phys. Soc. 1903-05, xix. pp. 114-156 (11/3/04); and Phil. Mag. ser. 6, vii. pp. 504-542 (May 1904).

† Hopkinson and Williams, "The Elastic Hysteresis of Steel," Proc. Roy. Soc. A, lxxxvii. pp. 502-511 (13/12/1912); Rowett, "Elastic Hysteresis in Steel," *ibid.* A, lxxxix. pp. 528-543 (2/3/1914); Kimball, "Measurement of Internal Friction in a Revolving Deflected Shaft," Gen. Elec. Rev. xxviii. pp. 554-558 (Aug. 1925); Kimball and Lovell, "Internal Friction in Solids," Mech. Engineering, xlix. pp. 440-442 (May 1927), and Phys. Rev. I. pp. 948-959 (Dec. 1927); Canfield, "Internal Friction in Metals," Phys. Rev. xxxii. pp. 520-530 (Sept. 1928).

however, showed large and systematic divergences from this law, and it was definitely discarded" (p. 168).

Although Kimball is now of the opinion that some of the phenomena observed by Newkirk and himself were due to another cause discovered later, and although his quantitative theory may be disregarded as based on assumptions (the same as Dr. Howland's) which he himself found to be false when he made measurements of elastic hysteresis, his main conclusion that elastic hysteresis and cramping fits may, and often do, cause whirling in a shaft running above its critical speed is most certainly correct. The present writer has watched the phenomenon too often to admit the slightest doubt of its existence.

Dr. Howland is again in error when he states that a permanent external force is necessary to bring hysteresis into play; all that is required is that there should be a bend in the shaft which does not rotate at the same speed as the shaft itself, so that the material is subject to an alternating strain.

Any accidental disturbance of the shaft from its position of equilibrium under the action of the main whirling forces will produce a transient whirl *which rotates at the critical speed*. When the shaft speed is higher than this the elastic hysteresis gives a driving force maintaining this whirl, and if this force exceeds the friction opposing the transient whirl that transient will grow until the shaft strikes the stops.

In his paper on "Shaft Whipping"\* Newkirk explains how he measured the actual rotation of the whirl by means of an oscillograph, and states that he always found it equal to the critical speed and in the direction of rotation of the shaft.

Feb. 24th, 1932.

### LXXXI. On Oberbeck's Vortices.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

I SHALL be obliged if you will kindly publish the following reply to the comments on section 7 of our paper † "On Oberbeck's Vortices" made by Messrs. Rutherford and Caldwell in the December 1931 issue of the 'Philosophical Magazine,' pp. 1190-1191.

\* Gen. Elec. Rev. xxvii. pp. 169-178 (March 1924).

† Phil. Mag. xi. pp. 1057-1081 (May 1931).

The method adopted by us in this section is admittedly approximate. The rigorous hydrodynamical equations are too complicated, and it is impossible to obtain a solution. We had therefore necessarily to simplify the equations by making suitable assumptions. The problem is to determine the motion of a jet of water forcing its way through still water. There is a discontinuity of motion at the boundary between the "jet" and the "still water." All the equations written in section 7 refer to the "jet" and not to "still water." Initially no element of fluid in the jet has rotation. It is the interaction of "still water" and the "jet" that introduces rotation in the latter. Had there been no "still water" the jet would have merely traced a parabolic trajectory, and would not have developed into "spiral vortices." We therefore made the assumption that the forces producing rotation in the jet are due to an extraneous agency, namely, the "still water," and should therefore be included in the force terms ( $X, Y$ ). It was further assumed that the rotation

$$\zeta = \frac{\partial v}{\partial y} - \frac{\partial u}{\partial x},$$

which was initially zero for each element of fluid in the jet, continued to remain so throughout the motion. This step was supported by equation (9); because this equation shows that the rotation  $\zeta$  involved in the "inertia terms" and the rotation  $\lambda$  in the "force terms" enter into the hydrodynamical equations in the same way. Unless therefore one of them be assumed to be zero, we would be taking account of the "rotation" twice in our equations. As in this case the rotation is produced by an extraneous agency the assumption  $\zeta=0$  would appear to be the most logical one. The comment that equation (10) "will certainly not be fulfilled for a fluid with friction" is tantamount to that "stream line" motion is impossible in a fluid with friction, and would thus appear to be absurd.

At any instant the velocities at the different points on a transverse section of the jet may be regarded as more or less constant. The internal viscosity of the fluid within the jet is negligible. The viscous forces, however, come into play at the boundary between the "still water" and the "jet." The viscous resistances introduced by "still water" to the motion of the jet are plainly extraneous forces. We therefore make the simple assumption, as is usually done, that such forces are proportional to the velocity at any point

of the jet. There is nothing in this assumption which goes against the rigorous equations of hydrodynamics. For incompressible fluid the rigorous equations are

$$\frac{Du}{Dt} = X - \frac{1}{\rho} \frac{\partial p}{\partial x} + \nu \nabla^2 u, \quad \frac{Dv}{Dt} = Y - \frac{1}{\rho} \frac{\partial p}{\partial y} + \nu \nabla^2 v.$$

It is known\* that the term  $\nu \nabla^2 u$ , due to viscosity, gives a variation of  $u$  "following the same law as that of temperature in thermal conduction or of density in the theory of diffusion. This variation is, in fact, proportional to the (positive or negative) excess of the mean value of  $u$  through a small sphere of given radius surrounding the point  $(x, y, z)$  over its value at that point." It is clear that if we draw a small sphere having its centre at any point of the boundary between "still water" and "jet" then at its centre  $u=0$  and within the portion of the sphere in the jet  $u=u$ . Therefore we can take the viscosity term  $\nu \nabla^2 u$  to be equal to  $-\nu \kappa^2 u$ ,  $\kappa$  being a constant, or simply  $-\mu u$ . Within the limit of approximation involved in this deduction equation (6) would appear to be quite correct. If a narrow stream of water in any transverse section of which the velocity is more or less uniform has to force its way through another fluid which is stationary it must experience viscous resistances approximately in the manner of equation (6).

There is no assumption involved in equations (11); they are merely steps leading to a solution of the dynamical equations as formulated under (9). The fact that

$$\tan \theta = \frac{v}{u} = \frac{V}{U}$$

is independent of  $t$  is in no way inconsistent with our photographs. It has to be remembered that the dynamical equations (9) refer to axes having an arbitrary origin but when substitutions of the kind (11) are made in them the axes have the "pole" of the equiangular spiral as the origin. This is clear from the subsequent solution, and particularly from the expressions for velocity given in (29). Since the pole is moving the direction of flow at any point fixed in space certainly changes with time, but at a point fixed relatively to axes passing through the pole, the  $x$ -axis being parallel to the axis of the jet, the direction of flow measured with reference to these axes does not change with time. This is what the expressions for velocity given in (29) mean, and is in agreement with our observations.

\* Lamb's 'Hydrodynamics,' fourth edition, p. 573.

In solving the equations we did assume that  $\lambda$  is uniform throughout the moving liquid, but stated that the solutions so obtained would be applicable over those regions where "this condition is strictly satisfied." The solution obtained on this assumption shows that the trajectory of the jet is a pair of equiangular spirals. If observations also show that the trajectory is a pair of equiangular spirals, then obviously  $\lambda$  is more or less uniform over the region covered by each of the spirals.

It is seen from equations (15) that  $\nabla^2 L = 0$  and  $\nabla^2 M = 0$ . The equation of continuity gives  $\nabla^2 \phi = 0$ . Therefore from the second equation of (14) we get  $\nabla^2 \psi = 0$ . Since  $L$ ,  $M$ ,  $\phi$ ,  $\psi$  are all harmonic functions, we see that the second equation of (14), namely,

$$M = (\mu - \alpha)\psi + \lambda\phi,$$

can be satisfied only if

- (1)  $M$  is a constant, and  $\phi$  and  $\psi$  are proportional to the same harmonic function,  
or, (2)  $M$ ,  $\phi$ ,  $\psi$  are all proportional to the same harmonic function.

Whether we choose (1) or (2) the result comes out to be of the same form as given in (16). There is therefore no loss of generality if we take the solutions of equations (15) in the form

$$L = f(t) \quad \text{and} \quad M = \text{constant}.$$

The omission of the arbitrary constant in (16) is of no consequence. It is omitted because it does not affect any of the subsequent steps.

In (13) we express  $(U, V)$  in the form

$$U = \frac{\partial \phi}{\partial x} + \frac{\partial \psi}{\partial y}, \quad V = \frac{\partial \phi}{\partial y} - \frac{\partial \psi}{\partial x}.$$

It is definitely known that when the components of velocity are expressed in this form  $\phi$  is not the "velocity potential" nor is  $\psi$  the "stream function."  $Udx + Vdy$  is not a perfect differential, even if  $\phi$  is proportional to  $\psi$  as is given in (16), and therefore no velocity potential can exist. Equation (21), just like (16), is merely a functional relationship between  $\phi$  and  $\psi$ . This equation does not make  $\phi$  a "velocity potential" or  $\psi$  a "stream function." According to analytical geometry the curves

$$\psi - \frac{\lambda}{\mu - \alpha} \phi = \text{constant}$$



must intersect the curves

$$\phi = \text{constant}$$

at a constant angle. The orthogonality of the functions  $\phi$  and  $\psi$  as expressed in (21) does not affect this angle of intersection in any way. The angle  $\epsilon$  in equation (24) cannot be equal to  $\frac{\pi}{2}$  unless  $\mu = \alpha$ . Equation (28) does not therefore become  $r = \text{constant}$ . The jet must therefore have the form of double equiangular spirals at any instant.

The mathematical theory is undoubtedly approximate, the more so because the motion in any section through the axis of the jet has been regarded as two-dimensional; but it will I hope be clear from what has been written above that it has none of the defects stated by Messrs. Rutherford and Caldwell. The agreement between the results deduced from it and the experiments is so close in all the essential details that it is certainly not fair to ascribe it to mere coincidence.

The Observatory,  
Bombay.  
January 3, 1932.

I am, Gentlemen,  
Yours faithfully,  
S. K. BANERJI.

## LXXXII. *Notices respecting New Books.*

*Monographs on Biochemistry: The Glycosides.* By Dr. E. F. ARMSTRONG, F.R.S., and K. F. ARMSTRONG. (London: Longmans, Green & Co., 1931. Price 12s. 6d. net.)

THIS work is based on a section of the well-known monograph 'The Simple Carbohydrates and the Glucosides,' written several years ago by the senior author. It affords a valuable account of our present knowledge of the chemistry of the "glucosides," and embodies much of the very latest work in this field. This is specially the case in Chapter III., which deals with the soluble plant pigments and contains a useful summary of various aspects of the researches of Robinson and his school, including the synthesis of anthocyanins and work on the position of the sugar molecule.

The term "Glycosides" does not meet with approval from all chemists, although it serves as a general name for the compounds yielding sugars (mannose, rhamnose, galactose, as well as glucose) and hydroxylic compounds on hydrolysis. Glucosides, therefore, form a special division of the class of glycosides. Still less euphonious and contrary to usual chemical nomenclature is the term "aglucone," suggested by Japanese workers for the non-sugar portion of the glycoside molecule. This may be an alcohol, a



phenol, an isothiocyanate, or a cyanohydrin, but rarely, if ever, a simple ketone, which is what the term would naturally imply.

The opening chapter pays homage to the pyranose and furanose formulæ for the sugars, but the older and now discarded term  $\gamma$ -sugar is occasionally met with.

In connexion with the cyanophoric or cyanogenetic glycosides (both terms are used) details are given of the many different factors, *e.g.*, temperature, humidity, stage of development, and cultivation (as distinct from "wild" growth), which affect the amount of hydrocyanic acid produced by the plant. This is obviously of economic and toxicological importance. Acetone cyanohydrin occurs combined with glucose as linamarin or phaseolunatin in young flax-plants and the seeds of the rubber-tree. It has been suggested that this acetone is the precursor of isoprene, from which not only rubber but most ingredients of essential oils may be derived. The importance of acetone in biochemistry is undoubted; it occurs also in the diabetic animal as a product of the bacterial decomposition of carbohydrate, and arises from aliphatic acids by the action of moulds.

The recent work of Baker and Robinson on the isoflavone glucosides also finds a place in Chapter III. This class of compound has only recently been recognized among natural products. Attention is drawn to the interesting formation of malonic acid on hydrolysis of the anthocyanin monardein occurring in golden balm. The malonic acid is attached through the sugar portion of the molecule. The work of Raistrick and his collaborators on mould fermentation is mentioned in Chapter I.; reference might be made here, however, to Raistrick's isolation from cultures of *Penicillium luteum* of luteic acid, which also gives glucose and malonic acid on hydrolysis. Other micro-organisms can also produce malonic acid.

Reference is also made to the recent observation that certain anthocyanins yield *p*-hydroxycinnamic acid and *p*-hydroxybenzoic acid on hydrolysis. It may be mentioned that *p*-methoxycinnamic acid is also obtained on hydrolysis of yangonin, another  $\gamma$ -pyrone derivative of plant origin.

The last two chapters deal with the function of glycosides and the utilization of carbohydrates in plants. They will be valuable to those who propose to investigate changes occurring during the storage and ripening of fruits.

An excellent bibliography, which has come to be regarded as a feature of this series of monographs, greatly enhances the usefulness of this valuable work.

*The Nature of Physical Theory: a Study in Theory of Knowledge.*

By VICTOR F. LENZEN, Ph.D. [Pp. 295 + xii.] (New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd., 1931. Price 21s. net.)

THIS book is an attempt to expound systematically how physical theory has developed by successive definition and approximation. The process of development is envisaged as follows:—There is an

abstraction of concepts from experience, a discovery and expression of laws in terms of the concepts, a redefinition of the original concepts to a higher order of approximation with increasing precision in the definition of conditions, a redefinition of new concepts in terms of the laws, and finally a reinterpretation of the original concepts in terms of the new.

After an examination of the basic concepts—space, time, body, quantity, etc.—the author proceeds to a survey of the methods, principles, and systems of physical theory. In this section, which covers some three-quarters of the book, there is given, within the limits which brevity imposes, an eminently clear and readable account of theoretical physics. The treatment of the geometrical conception of nature is particularly attractive.

To the earnest student of physics as well as to the experimenter, who are only too often unable to see the wood for the trees, such a survey should provide a valuable bird's-eye view.

The analysis of the fundamental concepts with which the book opens, and the discussion of methodological principles with which it concludes, though stimulating and refreshingly free from philosophic jargon, would gain in force and clarity by some ruthless pruning of repetitions.

A useful list of references is appended to most of the chapters, an adequate index is provided, and the typography is excellent.

*Theoretical Physics.* By W. WILSON, F.R.S.—Vol. I. *Mechanics and Heat* (NEWTON-CARNOT). [Pp. 332, 80 diagrams. Boards.] (London: Methuen & Co., 1931. Price 21s. net.)

THIS volume is the first of three which purpose to present an account of the theoretical side of Physics particularly intended for teachers and students.

In this first volume Mechanics and Heat are presented, with appropriate introductory chapters on Euclidean and Vector Analysis, the theorems of Gauss, Green, and Stokes, followed by useful chapters on Dynamics, Hydrodynamics, and Electricity. Chapters on Kinetic Theory, Thermodynamics, and, of course, Statistical Mechanics complete the volume.

It is made clear in the preface that the author aims at treating the subject on broad historical lines, with the result that the first volume is necessarily "entirely classical"; moreover, the mathematical treatment is kept within the limits set by a reasonable mathematical equipment. Special mathematical methods, where employed, are given special explanatory attention.

The book is likely to be of considerable value to the earnest student of Physics at the University. The title is perhaps a shade misleading, in that the subject of Heat, as dealt with in this volume, is confined within the region of Thermodynamics and Kinetic Theory; but this is a small matter of criticism in view of the generally good character of the book.

It is well printed, and the considerable mathematical reproduction is very pleasing.

LXXXIII. *Proceedings of Learned Societies.*

## GEOLOGICAL SOCIETY.

February 10th, 1932.—Prof. E. J. Garwood, M.A., Sc.D.,  
F.R.S., President, in the Chair.

Prof. S. JAMES SHAND, D.Sc., Ph.D., F.G.S., delivered a lecture on 'The Reaction between Granitic Magma and Limestone at Palabora, Transvaal.'

The Lecturer said that the Palabora granite is intrusive among ancient schists which include bodies of crystalline limestone. The hill Lulu Kop is a mass of metamorphosed dolomitic limestone isolated in the granite. Between granite and limestone there is a belt of flat ground, up to 2 miles wide, within which all the rocks exposed are rich in diopside and apatite; they vary from shonkinite to pyroxenite and massive apatite. Between these rocks and the granite there is a narrow belt of diopside-arfvedsonite-syenite. The evidence indicates extensive reaction between granitic magma and limestone, producing syenite and shonkinite, and it is suggested that the pyroxenite was formed by the sinking of diopside crystals from the contaminated magma. As assimilation of limestone went on, soda seems to have been progressively expelled from the magma, for in the shonkinite the only felspar is a highly potassic microcline. No nepheline is found at the present level, but there is a possibility that the expelled soda may have formed nepheline-rocks at higher levels, now removed by erosion.

The following communication was read :—

'The Lavas of Mauritius.' By Prof. S. James Shand, D.Sc., Ph.D., F.G.S.

The lavas of Mauritius are mainly basalts, some rich in olivine and others almost or quite free from it. No feldspathoids have been detected, but some of the rocks are of the 'pacificite' type, having nepheline in the norm. Soda-trachyte was found at two localities, and must be regarded as a differentiate of the basaltic magma. This rock, too, holds normative nepheline and is not far from a true phonolite. The problem of deriving phonolite from a basaltic magma is briefly discussed.

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[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

FIG. 5.

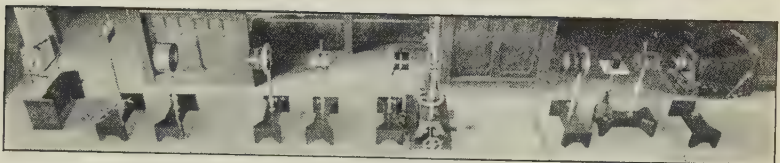


FIG. 6.

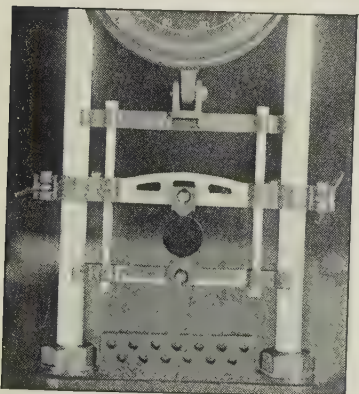


FIG. 7.



FIG. 8.

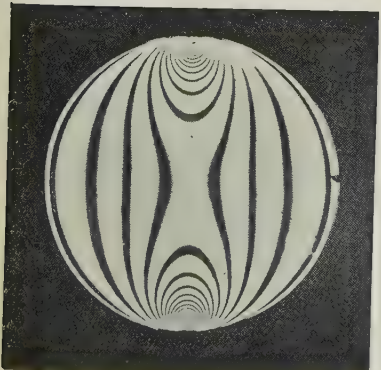


FIG. 9.







FIG. 10.

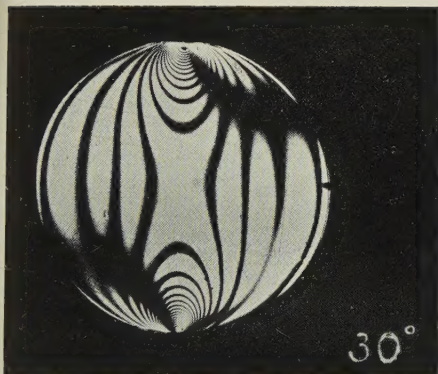


FIG. 16.

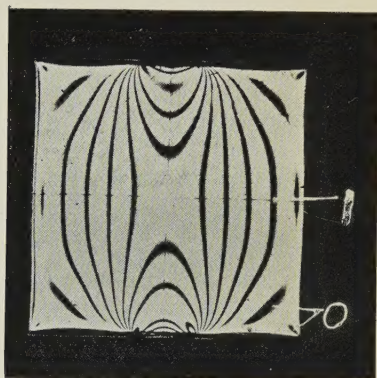


FIG. 17.

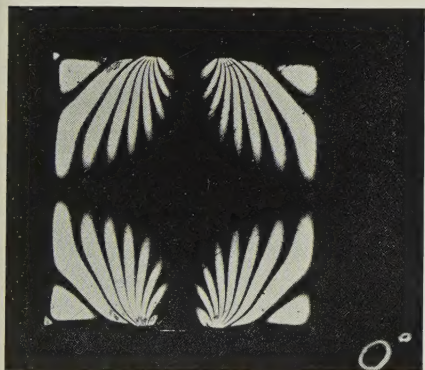


FIG. 18.

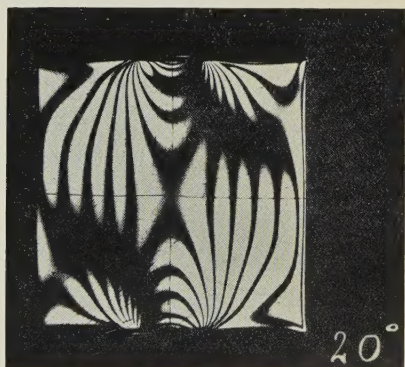


FIG. 19.

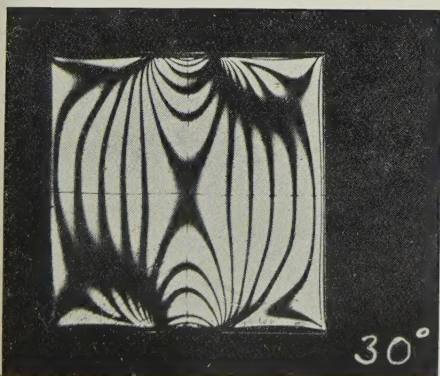


FIG. 20.

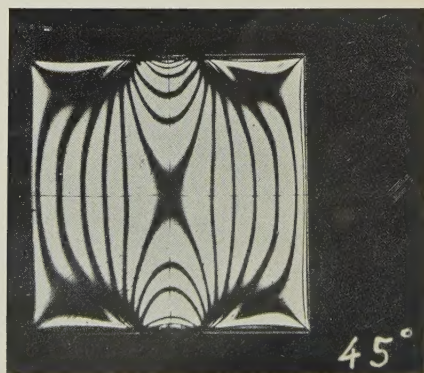






FIG. 10.

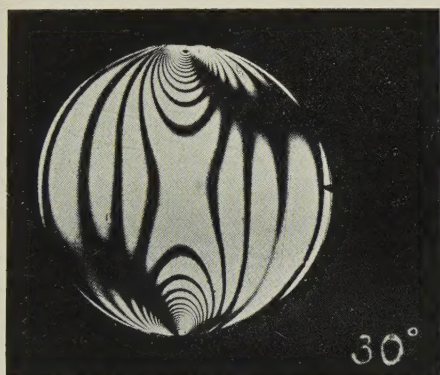


FIG. 16.

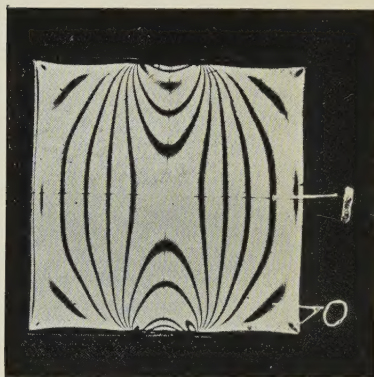


FIG. 17.

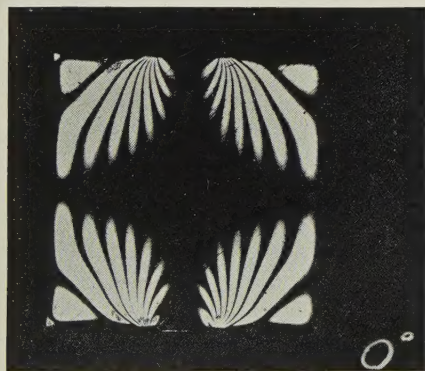


FIG. 18.

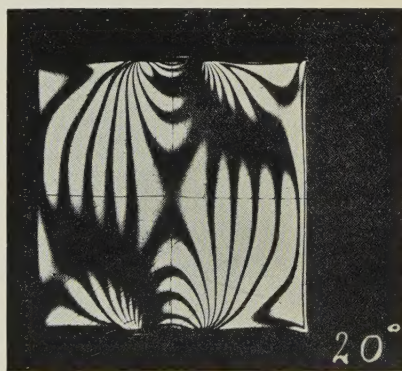


FIG. 19.

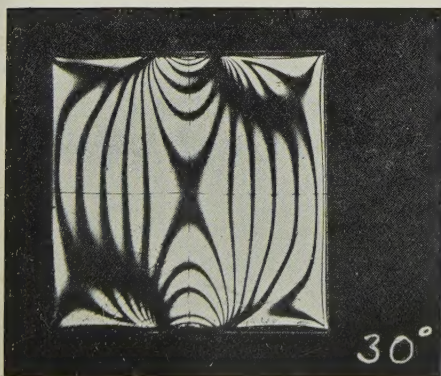


FIG. 20.

